The Application of Heritage Science in Cultural Heritage Management: End User Research

Jo Willey

A thesis submitted in fulfilment of the requirements of the University of Lincoln for the Degree of Master of Science by Research in Forensic Heritage Science

This research was carried out in collaboration with the University Museum of Bergen at the University of Bergen

May 2014

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Abstract

The subject of this Research Master of Science (MSc) carried out in the Science Faculty at the University of Lincoln is the application of heritage science in cultural heritage management. Within this broad area, the focus is on practical end user research that contributes to the interpretation, documentation and conservation of cultural heritage objects. The aim of the Research MSc was to address gaps in current knowledge and practice in the heritage sector identified in the U.K. National Heritage Science Strategy reports in 2009-2010, as well as specific questions that came up in conservation projects at the University Museum of Bergen in Norway prior to carrying out the Research MSc. The results of two research components are presented in the thesis. The first consists of the characterisation of a collection of modern religious medals from the University Museum of Bergen using portable X-ray fluorescence spectroscopy (pXRF) combined with environmental scanning electron microscopy-energy dispersive X-ray spectroscopy (ESEM-EDX) mapping and stereo microscopy. The research was carried out in collaboration with the Director of the University Museum of Bergen, Professor Henrik von Achen, who is also the Senior Curator for the Coins and Medals collections. The experimental work in this research component was designed to illustrate the way that the materials analysis of cultural heritage objects provides information that increases our understanding of the objects and contributes to their documentation, as well as informs the decision making process for their conservation and long term preservation. By combining complementary analytical techniques it was possible to identify different types of plated and non-plated metal alloys used to produce the modern religious medals, and in particular distinguish between the alloys used for the numerous white metal medals in the collection. The information gained facilitates the inclusion of the modern religious medals in the online catalogue of the coins and medals collections at the University Museum of Bergen. The second research component consists of analysing the effects of cleaning treatments in metals conservation using ESEM images and EDX analysis combined with pXRF analysis. The experimental work was designed to provide a visual database or atlas of the effects of a range of chemical and abrasive cleaning treatments on the surface of silver, copper, lead and iron coupons. The ESEM-EDX analyses indicated that there were significant changes in the metal surfaces after chemical cleaning treatments compared with the milder abrasive cleaning treatments. The results demonstrated the importance of assessing the pH of chemical solutions and the hardness of abrasive materials used in comparison with the hardness of the metal being treated before carrying out irreversible treatments such as cleaning. This practical end user information contributes to the decision making process for implementing appropriate

treatments in the conservation and long term preservation of cultural heritage objects with metals components made of silver, copper, lead and iron and in particular historic objects.

Acknowledgements

I would like to acknowledge and thank the following people for their assistance and support in carrying out this Research Master of Science.

Professor Belinda Colston and Dr Adrian Goodman in the Science Faculty at the University of Lincoln, as my supervisors for their help with the experimental work and organising the necessary materials and equipment in the Science Building. I would also like to thank Professor Colston for her comments while preparing the results of the first research component in this thesis for an oral presentation at the International Council of Museums (ICOM) Metal 2013 conference and publication in the conference proceedings.

Professor Henrik von Achen, Director of the University Museum of Bergen at the University of Bergen, Norway and Senior History Curator at the University Museum of Bergen for his generosity in collaborating on this Research MSc and providing access to the museum's collection of modern religious medals, as well as his contribution to the ICOM Metal 2013 conference paper on the non-invasive characterisation of the modern religious medals using portable X-ray fluorescence spectroscopy.

Associate Professor Frode Storås, Senior Anthropology Curator at the University Museum of Bergen, University of Bergen, Norway for his support and generosity in carrying out the Research MSc.

Angela Murtagh and Beverly Shepherd, Technical Staff in the Science Faculty at the University of Lincoln for their assistance with materials and equipment in the Science Building used in the Research MSc and generosity with their time.

Jannen Contreras, MSc student in Forensic Heritage Science in the Science Faculty at the University of Lincoln and Cultural Heritage Objects Conservator, for useful discussions about metals conservation.

Tom Atherton, PhD student in Forensic Science, Ami Pass and Nicky Bunting, PhD students in Forensic Heritage Science in the Science Faculty at the University of Lincoln for their assistance with the equipment in the Science Building used in this Research MSc.

Dr David Sommerfeld, Postgraduate student in the Archaeological Conservation Masters Programme at Durham University for his help with the statistical analysis involved in the experimental work and valuable comments on the experimental work carried out in the thesis.

Nick Barrett and John Hurley at Niton UK Ltd for information about the Thermo Scientific Niton XL 3t portable energy dispersive X-ray fluorescence (EDXRF/pXRF) analyser and its application in the analysis of historic metal objects.

Laura Pearson at the University of Lincoln Library for her help with the mathematical and statistical analysis of the experimental data and references on this in the library.

Denise Bateman and Professor Jonathan Cooper in the Science Faculty and Stephen Gilliatt in Student Records at the University of Lincoln for their assistance with the administration side of the Research MSc.

Henning Schulze, Senior Lecturer and Programme Leader for the BA Honours course in the Conservation Training Programme at the University of Lincoln, for useful discussions on the different approaches to surface cleaning treatments in historic metals conservation.

My family for their support and patience while I've been combining this part time Research MSc with part time Objects Conservation work.

Abbreviations

AATA Online	Abstracts of International Conservation Literature, The Getty Conservation Institute
AIC	American Institute for Conservation of Historic and Artistic Works
AICCM	Australian Institute for the Conservation of Cultural Material
CAC	Canadian Association for Conservation of Cultural Property
CAPC	Canadian Association of Professional Conservator
CCI	Canadian Conservation Institute
CHIN	Canadian Heritage Information Network
CIN	Conservation Information Network
CoOL	Conservation Online: Resources for Conservation Professionals
Cons DistList	Conservation DistList Archives
CSH	Centre for Sustainable Heritage, University College London
ECCO	European Confederation of Conservator-Restorers' Organisations
EPSRC	Engineering and Physical Sciences Research Council, U.K.
ESEM-EDX	Environmental scanning electron microscopy - energy dispersive X-ray spectroscopy
FTIR	Fourier Transform infra red spectroscopy
GCI	The Getty Conservation Institute
ICCROM	International Centre for the Study of the Preservation and Restoration of Cultural Property
ICOM-CC	International Council of Museums – Committee for Conservation
ICOMOS	International Council on Monuments and Sites
ICON	Institute of Conservation, U.K.
IIC	International Institute for Conservation of Historic and Artistic Works
NHSS	National Heritage Science Strategy, U.K.
PEL	Preservation Equipment Ltd., U.K.
pXRF	Portable X-ray fluorescence spectroscopy
RS	Raman spectroscopy
UCL	University College London
VPSEM	Variable pressure scanning electron microscope
XRF	X-ray fluorescence spectroscopy

Definitions

The terms used in the Research MSc thesis are based on definitions given in the U.K. National Heritage Science Strategy (NHSS) reports in 2009-2010, and publications by international conservation institutions and organisations, such as the European Confederation of Conservator-Restorers' Organisations (ECCO); International Council of Museums-Committee for Conservation (ICOM-CC); International Centre for the Study of the Preservation and Restoration of Cultural Property (ICCROM); Australian Institute for the Conservation of Cultural Materials (AICCM);Institute of Conservation, U.K. (ICON); International Institute for Conservation of Historic and Artistic Works (IIC); Canadian Conservation Institute (CCI) and Getty Conservation Institute (GCI).

Conservation

Conservation consists mainly of direct action carried out on cultural heritage with the aim of stabilising condition and retarding further deterioration (ECCO, 2002).

Conservator-Restorer

The fundamental role of the Conservator-Restorer is the preservation of cultural heritage for the benefit of present and future generations. The Conservator-Restorer contributes to the perception, appreciation and understanding of cultural heritage in respect of its environmental context, significance and physical properties (ECCO, 2002).

Cultural Heritage /Cultural Material/Cultural Property

Anything or concept considered of aesthetic, historical, scientific or spiritual significance (ICOM Code of Ethics, 2004).

Objects that are judged by society, or by some of its members, to be of historical, artistic, social or scientific importance. Cultural property can be classified into two major categories:

1. Movable objects such as works of art, artifacts, books, archival material and other objects of natural, historical or archaeological origin.
2. Immovable objects such as monuments, architecture, archaeological sites and structures of historical or artistic interest (CAC and CAPC, 2009).

Heritage Science

The term used to encompass all technological and scientific work that can benefit the heritage sector, whether through improved management decisions, enhanced understanding of significance and cultural value or increased public engagement (NHSS Report 1, 2009).

The Heritage Sector

The heritage sector in the U.K. consists of a number of independent sub-sectors. The main subsectors identified are movable and immovable heritage, where movable heritage consists of museums, galleries, libraries and archives, whereas immovable consists of the built historic environment and archaeology (NHSS Report 1, 2009).

Interventive Conservation/Remedial Conservation/Treatment

All actions directly applied to an item or a group of items aimed at arresting current damaging processes or reinforcing their structure. These actions are only carried out when the items are in such a fragile condition or deteriorating at such a rate, that they could be lost in a relatively short time. These actions sometimes modify the appearance of the items (ICOM-CC, 2013).

Preservation

The protection of cultural property through activities that minimise chemical and physical deterioration and damage, and that prevent loss of information. The primary goal of preservation is to prolong the existence of cultural material (AICCM Code of Ethics, 2002).

Preventive Conservation

Preventive Conservation consists of action to retard deterioration and prevent damage by creating conditions optimal for the preservation of cultural heritage as far as is compatible with its social use. Preventive conservation encompasses correct handling, transport, use, storage and display. It may also involve issues of the production of facsimiles for the purpose of preserving the original (ECCO, 2002).

Restoration

Restoration consists of direct action carried out on damaged or deteriorated cultural heritage with the aim of facilitating its perception, appreciation and understanding, while respecting as far as possible its aesthetic, historic and physical properties (ECCO, 2002).

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1.0 Introduction

The subject of this Research Masters of Science (MSc) carried out in the Science Faculty at the University of Lincoln is the application of heritage science in cultural heritage management. Within this broad area, the focus is on practical, end user research that contributes to an increased understanding and more accurate documentation of cultural heritage objects, as well as to the decision making process for their conservation and long term preservation. The end users for the research would primarily be Curators, Curatorial Assistants, Art Historians, Conservators and Conservation Scientists working in museums, galleries, libraries, archives and other institutions with collections of cultural heritage objects.

The aim of the Research MSc was to address specific questions in the documentation and conservation of cultural heritage objects, thereby providing practical information that contributes to their collections management and conservation. The specific questions addressed were based on gaps identified in current knowledge and practice in heritage science in the U.K. by the National Heritage Science Strategy (NHSS) reports in 2009 and 2010 (Williams, 2009a; NHSS Steering Group, 2010), in combination with questions that came up in my work as an Objects Conservator at the University Museum of Bergen at the University of Bergen in Norway, prior to starting the Research MSc. The objectives were to contribute to the understanding of the materials cultural heritage objects are made of through non-invasive analysis and improve current conservation practice by analysing the effects of treatments carried out on cultural heritage objects.

The Research MSc therefore consists of two components or case studies designed to illustrate the practical application of heritage science in cultural heritage management and address these gaps in current knowledge and practice. The first research component consists of the non-invasive analysis of a collection of modern religious medals made of a diverse range of metal alloys, using portable X-ray fluorescence spectroscopy (pXRF), combined with environmental scanning electron microscopy coupled with energy dispersive X-ray spectroscopy mapping (ESEM-EDX) and stereo microscopy. The second research component consists of analysing the effects of different types of cleaning treatments in metals conservation on the surface of coupons of silver, copper, lead and iron alloys using ESEM-EDX, combined with the elemental analysis of the control coupons for each type of metal using pXRF. This combination of analytical techniques was employed to illustrate the way heritage science research can be carried out using equipment and methods that are appropriate in

terms of accuracy and precision for the question(s) being asked, as well as the resources available and provide information that can directly assist in the decision making process for the conservation and long term preservation of cultural heritage objects.

The experimental work for the research components was also intended to be presented to those working in the heritage sector and published in relevant printed and electronic journals, so that the practical end user information gained can be disseminated. This has included presenting the results of the ESEM-EDX analysis of the effects of cleaning treatments in metals conservation to students in the Conservation Training Programme at the University of Lincoln, and the preparation of a presentation and forthcoming publication of the results of the non-invasive pXRF analysis of the modern religious medals for the International Council of Museums (ICOM) Metal 2013 conference.

The first part of the Research MSc thesis consists of a literature review on the application of heritage science in cultural heritage management in Section 2.0, starting with the NHSS reports from 2009 and 2010, followed by a discussion of references for the two research components. The analytical techniques used and the experimental procedure for the two research components are documented, followed by a discussion of the results, conclusions and recommendations for future research in Sections 3.0 and 4.0. The references are listed in Section 5.0, followed by the digital photographs and experimental data for the two research components in the appendices in Section 6.0. Lastly the materials and suppliers for the research MSc are documented in Section 7.0.

2.0 Literature Review

2.1 U.K. National Heritage Science Strategy (NHSS) Reports 2009-2010

The literature review started with general references on the application of heritage science in cultural heritage management, in printed and electronic cultural heritage and scientific publications, as well on the websites of international heritage organisations, museums, galleries, libraries and archives. The idea was to gain an understanding of current directions in heritage science and its application in conservation projects which contribute to the collections management of cultural heritage objects. The series of NHSS reports written in 2009 and 2010 and available online on the Science and Heritage Programme website of the Centre for Sustainable Heritage at the University College London (UCL) were particularly significant, due to their relatively recent publication date and the comprehensive discussion of the state of heritage science in the U.K. The NHSS reports were written in response to recommendations made in the House of Lords Science and Technology Committee inquiry into heritage science in the U.K. in 2006, and aimed to provide evidence based information for developing a sustainable strategy for heritage science in the U.K.

The first NHSS report entitled 'The Role of Science in the Management of the U.K.'s Heritage' (Williams, 2009a) provides an introduction to the heritage sector in the U.K. The different sub-sectors within cultural heritage are outlined and definitions given for different types of cultural heritage, with the distinction made between movable and immovable heritage. Movable heritage is defined as collections in museums, galleries, libraries and archives, while immovable heritage is defined as the built historic environment and archaeological sites. This was followed by a discussion of gaps in current knowledge and practice in heritage science in the U.K. Two areas identified as requiring further heritage science input were:

- Understanding material behaviour through non-invasive analysis, particularly modern materials
- Improving practice through a greater understanding of the effects of treatments currently used in the conservation of cultural heritage.

(Williams, 2009a: 25-33)

The second NHSS report entitled 'The Use of Science to Enhance Our Understanding of the Past' (Williams, 2009b) discusses the types of scientific techniques that can be used to answer questions about cultural heritage and contribute to our understanding of the past. The conclusions included the recommendation that heritage science research should focus on

addressing practical, end user questions and contribute to the increased involvement and understanding of cultural heritage by the general public. The third NHSS report entitled 'Understanding Capacity in the Heritage Science Sector' (Williams, 2009c) provides an overview of the academic background and training of heritage scientists, and identifies areas in the heritage sector where there is a lack of people to meet the current research needs. The fourth NHSS report entitled 'Our Vision and Strategy for Heritage Science' (NHSS Steering Group, 2010) summarises the previous three NHSS reports and puts together a strategy for the development of heritage science in the U.K. to enable it to keep up with international developments in the heritage sector. An increased use of science and technology in collaborative, cross-disciplinary projects is recommended to increase access to analytical equipment and demonstrate the value of heritage science to a wider audience.

The NHSS reports were a useful starting point for the Research MSc as they indicated directions to take with research that would provide practical information and contribute to the heritage sector in the U.K. By combining the recommendations made in the NHSS reports with collections-based questions that have come up in my work as an Objects Conservator, it was possible to narrow the focus of the Research MSc thesis to the following research components:
1: Materials analysis of modern cultural heritage such as the predominantly 20th century religious medals in the collection of the University Museum of Bergen in Norway.
2: Improving current conservation practice by analysing the effects of conservation treatments such as surface cleaning techniques in metals conservation.
By concentrating on these two areas of research, the aim was to illustrate the importance of materials analysis combined with the analysis of the effects of conservation treatments, as it provides information on the materials cultural heritage objects are made of and their interaction with the materials and methods used to treat them. This information can be directly incorporated in the decision making process for the long term preservation of cultural heritage objects.

2.2 Materials Analysis: The Non-Invasive Characterisation of a Collection of Modern Religious Medals using Portable X-ray Fluorescence Spectroscopy

As indicated in the NHSS reports, there is a relatively limited amount of published information on the analysis of modern materials such as the diverse range of modern metal alloys developed in the 20th century. This may be partly due to the way that modern metal alloys can be relatively inexpensive to produce and have been used in the mass production of cultural heritage objects which may have relatively less status compared to objects made of metals such as gold and silver. For example, objects such as the collection of approximately 20 000

modern European religious medals at the University Museum of Bergen. However questions about the composition of these kinds of objects and how to accurately document them remain, as does the need to make appropriate decisions about their conservation based on information about the types of metal alloys they are made of. The inclusion of the modern religious medals in the online catalogue of the coins and medals collections that is in the process of being prepared at the University Museum of Bergen has been hindered by a lack of information on the alloy types used to produce the medals, as has the implementation of preventive and interventive conservation procedures for their preservation. This was particularly the case with the large numbers of silvery grey or white metal religious medals in the collection, which can consist of a range of quite different metal alloys, such as silver plated copper-zinc alloys, copper-nickel alloys, silver-copper alloys, copper-zinc -nickel alloys and aluminium alloys.

One of the most comprehensive references on European religious medals is by Martini entitled 'Medaglia devozionale cattolica moderna e contemporanea in Italia ed Europa, (1846-1978), published in several volumes in 2009 in Italian, but this is unfortunately not as accessible as references in English. However it is clear that the extensive documentation of the European religious medals presented in this publication includes analysis of the medals using techniques such as XRF and SEM-EDX. Alloys such as copper-zinc and copper-nickel are identified and classified according to the ratio of zinc and nickel to copper, as well as by the colour of the alloys (Martini, 2009: Vol.1.2: 575-597).

Given the limitations in the reference material on modern religious medals and their analysis, the literature review included publications on the non-invasive analysis of other types of metal objects, as well as other types of inorganic cultural heritage such as obsidian, using the techniques of XRF and SEM-EDX; in particular XRF and pXRF as they have been used to analyse a wide range of cultural heritage. (Moioli and Seccaroni, 2000; Cesareo et al., 2007; Craig et al., 2007; Gianoncelli et al., 2007; McGlinchey and Trentelman, 2007; Harrison and Beaubien, 2011; van Langh et al., 2011; Smith, 2011; Goodale et al., 2012). The increasing use of XRF and pXRF to analyse cultural heritage is attributed to the advantages of the non-invasive nature of the analyses; developments in the analytical instrumentation such as thermo-electrically cooled detectors; the increased capacity of miniature X-ray tubes; the speed at which the analysis can be carried out; the relatively good analytical precision of the results for a range of elements and the versatility and relative low cost of the portable equipment (Craig et al., 2007: 2013-14, 2022; Goodale et al., 2012: 882).

References on the XRF and pXRF analysis of cultural heritage also discuss the disadvantages involved, given that it is a surface technique and there are limitations with accurately analysing inhomogeneous materials. For example, uneven surfaces on geological or mineral samples, corroded archaeological objects, and plated, patinated, heat treated, coated, corroded or tarnished metal objects (van Langh et al., 2011: 273). There can also be interference from certain types of detectors if appropriate filters are not used; inconsistencies in the instrument-surface distance with three dimensional objects or samples and a loss of sensitivity when using air path instruments (McGlinchey and Trentelman, 2007: 195). There are also limitations in the ability of pXRF to analyse low atomic number elements (Goodale et al., 2012: 882) and pXRF equipment is considered to be less accurate than the stationary laboratory-based XRF equipment. As a result of these limitations, caution is recommended when interpreting the results of XRF analysis and in particular pXRF analysis. The results of pXRF analysis are therefore generally considered to be semi-quantitative or qualitative.

Despite these limitations, instrument precision and consistency in the results of XRF and pXRF analyses have been reported when rigorous experimental procedures have been followed, such as regular calibration of the XRF equipment, comparison with known reference standards, reproducibility tests and an evaluation of instrument performance (Craig et al., 2007: 2020; Goodale et al., 2012: 880). An inter-laboratory study of the reproducibility of XRF analysis of historic copper alloys carried out by the Getty Conservation Institute in collaboration with a number of international museums and cultural heritage institutions (Heginbotham et al., 2011) indicated that use of certain types of detectors such as silicon drift detectors (SDD) or silicon-PiN diode detectors (PIN), and quantification methodology based on fundamental parameters software calibrated with reference standards were significant factors in increasing the accuracy of XRF analysis and achieving quantitative results. The inter-laboratory study also recommended including comprehensive documentation on the operating parameters used in XRF analysis, such as the voltage (kV), current (mA), measurement time, spot size, filters and the number of counts collected by the detector per second, as well as error factors and detection limits to facilitate the reproducibility and interpretation of the results. In addition the analysis of control samples of reference materials was recommended (Heginbotham et al., 2011: 246, 253).

2.3 Improving Conservation Practice: Analysing the Effects of Cleaning Treatments in Metals Conservation with Scanning Electron Microscopy - Energy Dispersive X-ray Spectroscopy

The need for further research on the effects of conservation treatments in use, in addition to research on developing new treatments, was recommended in the NHSS reports to improve current practice in the conservation of cultural heritage (Williams, 2009a; NHSS Steering Group, 2010). By investigating the interaction of the materials cultural heritage objects are made of with the materials and methods used to conserve them, the effectiveness of treatments can be assessed, as well as the possible loss of information as a result of the treatments. Both these factors have significant implications for the collections management of cultural heritage in terms of resources and preserving the integrity of the objects. One particular area of current practice that was identified in the NHSS reports as requiring further heritage science input was examining the effects of standard conservation treatments, such as surface cleaning, washing and the desalination of cultural heritage objects (Williams, 2009a: 33). This reflects an increasing awareness in conservation of the irreversible nature of treatments such as these and the possibility of losing information or the damaging long term effects due to the use of inappropriate materials and methods. Recent references in metals conservation suggest an ethical shift away from more invasive interventive treatments such as the chemical cleaning of objects towards alternatives such as mechanical cleaning in combination with the use of preventive conservation procedures, or localised chemical and electrochemical treatments for certain types of metal objects (Costa, 2001; Scott, 2002; Scott and Eggert, 2009). This is particularly evident in the conservation of archaeological metal objects (English Heritage, 2008).

Looking at the conservation literature, there are a number of publications on the effects of treatments over the last forty years, such as the articles on the effects of cleaning treatments used in metals conservation dating to the 1980's and 1990's. Many of these publications are still relevant today (Laver, 1980; North, 1980; Wharton et al., 1990; Selwyn and Costain, 1991; Selwyn, 1997), however there appears to have been limited access to some of these references, as questions regarding the use of metals conservation treatments that have been analysed continue to come up (Dixon, 2004). In addition, some interventive treatments known to have negative side effects such as the use of proprietary metal cleaning products, for example acidified thiourea silver dip solutions and metal polishes that contain ammonia continue to be recommended and used in conservation practice, in particular with historic metal objects (National Trust, 2006: 256, 318). The analysis of proprietary metal cleaning products such as silver dips and metal polishes carried out in the 1980's and 1990's

(Laver 1980; North, 1980; Wharton et al., 1990; Selwyn and Costain, 1991) and the subsequent recommendations limiting their use by museums and cultural heritage institutions such as the Canadian Conservation Institute (Selwyn and Costain, 1991; Selwyn, 1997, 2004) appear not to be well known or the risks involved in their use are possibly regarded as acceptable in the treatment of historic metal objects. Reasons for this may be the relative speed with which some proprietary products work and the relatively large size of many historic metal objects or collections of objects requiring treatment, as these factors can have an impact on the resources available for cultural heritage conservation projects in terms of time constraints, staff numbers and budgetary limitations.

Many of the analyses carried out in the 1980's and 1990's examined the loss of metals such as silver from the surface being cleaned, and indicated that the main problems with proprietary metal cleaning products used in metals conservation are the presence of abrasives that are too aggressive for use on certain types of metals, as well as the presence of chemicals that can lead to the deterioration of the objects being treated such as ammonia, sulphur, chlorine and silicon (North, 1980; Wharton et al., 1990; Selwyn and Costain, 1991; Selwyn, 1997 and 2004). Additional disadvantages involved in the use of proprietary products are that the formulations can be trade secrets and it can therefore be difficult to know exactly what they consist of, or the formulations can change over time without the consumer knowing. Therefore the use of proprietary products in the conservation of metal cultural heritage objects has been controversial for a number of years and is considered unethical in some circumstances (Selwyn and Costain, 1991: 4).

An alternative to the use of proprietary products is the preparation of materials for use in treatments in the conservation laboratory or studio. This approach has been favoured in recent years as the composition of the materials prepared is known and potentially damaging components such as ammonia, sulphur, chlorine and silicon can be avoided. Analysis of a range of laboratory prepared materials for treating metals such as silver has been carried out using techniques such as SEM-EDX (Wharton et al., 1990), and the results indicated that calcium carbonate, gamma alumina and chromium oxide prepared as abrasive pastes effectively remove silver tarnish and cause the least damage to the silver surfaces tested. Calcium carbonate has subsequently been recommended for cleaning silver in metals conservation, however the type of calcium carbonate is important as precipitated calcium carbonate is thought to cause less scratching of the silver surface than levigated calcium carbonate due to the finer particle size. The fine particle size of precipitated calcium carbonate can also cause

scratches, but these are considered to be acceptable as they are generally not visible without magnification (Selwyn, 1999).

The issues involved in the use of proprietary products versus conservation laboratory preparations for cleaning silver and the trend towards less interventive treatments also apply to the conservation of other types of historic metals such as copper, lead and iron alloys. However analysis of the effects of cleaning treatments on these types of metals is not as well represented in the literature as silver. The conservation of objects made of lead has received a certain amount of coverage, possibly due to the complications involved treating lead due to the relatively soft nature of the metal, which precludes the use of most mechanical treatments; the insoluble nature of some lead corrosion products, which can be harder than the lead metal, as well as the toxicity of working on lead. The use of localised electrolytic treatments for lead objects, such as the consolidative reduction of lead corrosion has been recommended as a result. The use of chemical treatments, such as acids and alkalis to remove lead corrosion are no longer recommended in recent references due to the possibility of damage to the exposed lead surface during treatment. However the application of dilute sequestering agents such as ethyl diamine tetra-acetic acid (EDTA) and disodium EDTA have been used with caution on some types of historic lead objects (Watson, 1985; North, 1987; Pearson, 1988; Cronyn, 1990; Costa and Urban, 2005; Schotte and Adriaens, 2006), as well as on copper corrosion(Huda, 2002).

The relatively recent publications on copper and iron alloys (Scott, 2002; Scott and Eggert (2009) provide a comprehensive overview of the metallurgy, corrosion, colorants and conservation of copper, bronze and iron alloys from marine, buried and ambient contexts. One of the main issues covered in the sections on the conservation of copper and iron alloys are the advantages and disadvantages of using chemical versus mechanical cleaning treatments. Due to the difficulty in controlling chemical treatments and the possibility of damaging the exposed metal surfaces or surface patinas during treatment, investigative mechanical treatments are recommended (Scott, 2002: 357-369; Scott and Eggert, 2009: 134-135), particularly for archaeological objects where the corrosion products may preserve associated organic materials. This is supported by other relatively recent publications on the investigative conservation of cultural heritage objects (English Heritage, 2008). The careful application of certain chemical treatments is however considered for some copper and iron alloys, as well as electrochemical treatments for iron. However the use of proprietary products in the treatment of copper and iron alloys is not as well covered in the literature on the conservation of historic copper and iron objects. In some cases the only available references

for the use of proprietary products on historic copper and iron alloys are the materials safety data sheets for the products, as these can provide information on the components in the products and indicate possible damaging effects on the metals being treated. However this kind of information is not always available as details of the components in some proprietary products are not published.

Therefore it appears that the use of proprietary products which can have damaging components such as ammonia, sulphur, chlorine and silicon or consist of aggressive abrasives and chemicals may not be well documented. A systematic analysis of the effects of different types of proprietary chemical and abrasive cleaning treatments versus laboratory preparations used in the conservation of metals such as silver, copper, lead and iron using SEM-EDX would provide direct, visual information about what happens to the surface of metals as a result of cleaning treatments. This information could then assist in the decision making process for the conservation and collections management of cultural heritage objects with metal components, in particular historic metal objects.

3.0 Non-Invasive Characterisation of a Collection of Modern Religious Medals using Portable X-ray Fluorescence Spectroscopy

3.1 Introduction

A group of 60 modern religious medals from a collection of approximately 20 000 in the University Museum of Bergen, at the University of Bergen in Norway was characterised using portable X-ray fluorescence spectroscopy (pXRF) in combination with environmental scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (ESEM-EDX) mapping and stereo microscopy in the Science Faculty at the University of Lincoln in the U.K. The aim of the analyses was to provide semi-quantitative and qualitative information on the types of alloys used in the modern religious medals, facilitating their inclusion in an online catalogue of the coins and medals collections at the University Museum of Bergen. Since many of the modern religious medals can be described as white metal, the non-invasive characterisation of the surface of the 60 medals was carried out to distinguish between silver plated copper alloys, 'nickel silver' alloys, silver-copper alloys, copper-nickel alloys and aluminium alloys. The medals were analysed in groups based on their stylistic type, with three readings on both sides of each medal. This procedure was repeated to indicate the reproducibility of the pXRF analyses, as well as to increase the data base on which conclusions about the alloys used in the religious medals could be made. Therefore the total number of pXRF readings on each side of the 60 medals was six.

ESEM-EDX mapping and stereo microscopy were carried out to complement the pXRF analysis by examining the presence of plating and corrosion products on the medals, given the limitations with the XRF technique in analysing inhomogeneous samples such as corroded, tarnished, plated, patinated and heat treated metal objects (van Langh et al., 2011: 273). The combined analytical results indicated a range of silver plated and non-plated alloys for the white metal medals and the other religious medals in the study group. Corrosion products such as chlorides and sulphides were indicated by the ESEM-EDX mapping, while inscriptions or text, as well as manufacturing techniques for the medals were examined with the stereo microscopy. The combined information contributes to a greater understanding of the modern religious medals and can be incorporated into the documentation of the collection at the University Museum of Bergen. Knowing more about the modern religious medals and the different types of alloys used to produce them also assists in the decision making process for their conservation and long term preservation.

3.2 The Collection of Modern Religious Medals at the University Museum of Bergen

In 2010 the University Museum of Bergen at the University of Bergen in Norway acquired a diverse collection of approximately 20 000 modern religious medals, which includes up to 7000 different examples. The religious medals were collected in Britain and are thought to have been in use there during the 20th century. They are therefore mainly dated to the 20th century up to the 1970's (von Achen, 2011). The exceptions include a number of medals dating to the second half of the 19th century, such as commemorative medals dated to a particular year. The majority of the religious medals are European, originating or intended for use in countries such as Italy, France, Germany and Britain, based on the languages other than Latin used in the inscriptions or text on the medals, as well as the inclusion of the name of a place or a country on some of the medals. In addition there are examples from the U.S. in the collection, as indicated by the inscriptions or text on the medals.

An extensive range of motifs are depicted on the modern religious medals, commemorating Christ, the Virgin Mary, saints, pilgrim sites, religious events or the reception of sacraments. They are intended to remind the wearer of their religious beliefs and strengthen their faith, as well as be used in devotional practices. The medals are usually quite worn, having been placed for years in wallets or pockets, attached to rosaries or worn around the neck of the faithful (von Achen, 2013). Regardless of their quality or material, many of the religious medals would have been blessed (Thurston, 1913). **Figure 1** shows a photograph of a woman wearing an oval-shaped religious medal on a chain around her neck, taken by the American photographer Paul Strand in the Outer Hebrides in Britain in 1954 (Duncan and Eskilden, 1994: 70).

Figure 1: Photograph taken in 1954 by the American photographer Paul Strand in the Outer Hebrides in Britain, showing a woman wearing an oval-shaped religious medal on a chain (Duncan and Eskilden, 1994: 70).

The mass production of these medals in the 19th and 20th century provided inexpensive items for use as instruments of devotion in the Catholic religion. By the 1830's and 1840's there was an increasing demand for them and large numbers of small religious medals were being made in Europe, in cities such as Paris, Lyon, Toulouse and Bordeaux in France; Rome, Torino, Milan, Florence, Naples and Parma in Italy; Bonn, Frankfurt am Main and Aachen in Germany; Brussels in Belgium and London in England (Ajmar and Sheffield, 1994: 41; Martini, 2009: 227-9). Between 1832 and 1837 alone it is estimated that over 21 million religious medals made of copper and silver of the type known as the Miraculous Medal were produced in Europe (Ajmar and Sheffield, 1994: 41). Considering the numbers of religious medals produced the most economic method of manufacture for them would have been striking between two die, as in the production of modern coinage. While the initial outlay for the setting up the required equipment and making the die would have been high, the costs would have been recovered by producing large quantities of the religious medals. One jeweller and die sinker working in Paris in the 1830's and known to have carried out numerous commissions for religious medals considered it was necessary to sell at least 200 000 religious medals to make a profit (Ajmar and Sheffield, 1994: 41). To minimise wear on the die and thereby keep costs down, the metal blanks and planchets used for the religious medals could be cast before striking, rather than cut or stamped from sheet metal during striking (Attwood, 2014). However casting may also have been used for some of the religious medals produced in more limited numbers, for example, under approximately 100, as casting is a less economical method of producing small metal items such as the religious medals (Attwood, 2014). By the 20th century striking prepared blanks or planchets between two steel die was a standard manufacturing technique in the mass production of modern coinage (Fleur-de-coin, 2014), and this manufacturing technique would also have been used for small metal items such as the religious medals. Therefore the majority of the religious medals in the collection of the University Museum of Bergen would have been struck from metal blanks or planchets that could have been cut from sheet metal or cast in the required shape.

The worn and abraded condition of many of the religious medals in this collection can however limit the visual identification of the manufacturing techniques used for some of the medals. Metallographic analysis of the microstructure of samples taken from the medals would provide definitive information on the way they were made; however this is a destructive analytical technique and the emphasis in this research component was on the non-invasive characterisation of the religious medals. As mentioned in the literature review, there is also

a lack of reference information published in English on the modern religious medals, including the techniques used to make them (von Achen, 2011; Attwood, 2014). Classification of the numerous stylistic types has not been well documented due to the extraordinary diversity in the religious medals and the numbers produced (New World Encyclopedia, 2013). The relatively low status of these medals in comparison with other metal objects could be another factor in the existing lack of information on the modern religious medals and their manufacturing techniques (von Achen, 2011). This paucity of information is one of the reasons why the Senior Curator for the Coins and Medals collections and Director of the University Museum of Bergen, Professor von Achen is planning to carry out a comprehensive social history project on the collection of modern religious medals. The analyses for the Research MSc were therefore carried out as a pilot study for the planned social history project, to see what information could be gained about the alloys used to produce the religious medals from the application of a combination of non-invasive analytical techniques used in heritage science.

The large numbers of silvery grey medals in the collection, which can be described as white metal were of particular interest. The appearance and condition of the white metal medals varies a great deal. Some appear to be silver plated with the base metal exposed on worn surfaces, others are tarnished or corroded with different coloured corrosion products and some are much lighter in weight; indicating a variety of metal alloys used in the production of the medals, such as silver plated copper alloys, nickel silver and aluminium alloys. To gain a better understanding of the different alloys used and accurately document the religious medals, the non-invasive characterisation of 60 medals was carried out using a Thermo Scientific Niton XL 3t portable X-ray fluorescence (pXRF) analyser. Due to the limitations involved in the analysis of plated, patinated, heat-treated, tarnished or corroded metals (van Langh et al., 2011: 273), the pXRF analysis was combined with a stereo microscopic examination of the 60 medals and environmental scanning electron microscopy-energy dispersive X-ray spectroscopy (ESEM-EDX) mapping of a number of medals to examine the presence of plating and corrosion products. These techniques were used to analyse the surface of the religious medals and were not intended to provide quantitative information on the elemental composition of the religious medals.

A study group of 60 modern religious medals were selected from the collection of approximately 20 000 with Professor von Achen, based on the stylistic types. There are numerous copies of the various stylistic types in the collection and the 60 religious medals chosen represent examples of the most common or typical types (von Achen, 2011). The earliest medals included in the study group are two commemorative medals dated to 1862

and 1897, and the most recent medals are thought to be dated to the mid 1970's (von Achen, 2011). In addition, one medal has the date 1950 on one side and a number of the medals have the same elongated oval shape as the one shown in the photograph in Figure 1, taken by Paul Strand in 1954 and may be of a comparable mid 20th century date. With regard to the provenance of the religious medals in the study group there are 29 medals with inscriptions or text in languages other than Latin, which may suggest their place of origin or intended use. Of these 29 there are 13 medals with text in English; four medals with text in French, another four with the word 'FRANCE' included on the medal and one with the word 'LYON'; five medals with the word 'ITALY'; one with the text in German and one with 'NEW HAVEN CONN.' included on the medal indicating it is from the U.S.

The following types were chosen for the study group of 60: 17 medals depicting Christ; 6 Infant of Prague medals; 21 Madonna and Child medals; 6 Blessed Sacrament medals and 10 Diverse medals with a distinctive appearance. Examples of each of these types are shown in **Figures 2 to 6.** Digital photographs of all 60 medals are included in section 6.1.1 of the Appendices. The medals selected do not appear to have been conserved or restored, which is typical of the collection in general.

Figure 2: Jesus Christ Medals 14, 16, 10 and 3 from left

Figure 3: Infant of Prague Medals 21, 23, 18 and 19 from left

Figure 4: Madonna and Child Medals 29, 33, 30 and 27 from left

Figure 5: Blessed Sacrament Medals 36, 34 and 37 from left

Figure 6: Diverse Medals 59, 57, 58 and 53 from left

Prior to the pXRF analysis a microscopic examination was carried out on each of the 60 medals using a Meiji EMT stereo microscope with 10-30x magnification and digital photographs were taken using an Olympus E620 camera and a copy stand. Individual conservation reports for the 60 medals were then prepared for the University Museum of Bergen which include the digital photographs of both sides of each medal; the dimensions and weight; a description of each side of the medals including information on the presence of surface plating, patination and coatings; manufacturing techniques; details of the condition such as tarnish or corrosion

products and a summary of the results of the pXRF analysis. A weight % (wt. %) range was given for the non-plated medals and medals that have highly worn surfaces with minimal or no plating remaining and exposed areas of base metal. While only the alloy type was given for the plated medals. These reports were designed to be directly incorporated in the museum's documentation of the coins and medals collections, and the combination of digital photographs with the pXRF results on the alloy types was intended to assist museum staff in becoming more familiar with the different types of alloys used to produce modern religious medals.

3.3 Objectives

The objectives of the non-invasive characterisation of the group of 60 modern religious medals were to combine pXRF analysis, ESEM-EDX mapping and stereo microscopy to provide semi-quantitative and qualitative information on the different types of plated and non-plated metal alloys used to produce the medals and facilitate their inclusion in an online catalogue of the coins and medals collections at the University Museum of Bergen. Specific questions addressed were to see if it was possible to distinguish between the different types of alloys used in the white metal medals, given the limitations involved in the pXRF analysis of inhomogeneous samples, as well as provide information that would contribute to the decision making process for implementing appropriate preventive and interventive conservation measures as part of the preservation and collections management of the modern religious medals at the University Museum of Bergen.

3.4 Analytical Techniques

3.4.1. X-Ray fluorescence Spectroscopy

X-ray fluorescence spectroscopy (XRF) is a non-invasive technique that analyses the elemental composition of the surface of materials. It has wide application in the heritage science sector where it has been used to analyse metals, obsidian, ceramics, glass, gem stones, inks, pigments and minerals, as well as to determine the thickness and composition of surface layers and coatings (Stuart, 2007: 234-243; Brouwer, 2010: 8). Samples can include solids, liquids and powders, and the objects or samples can be analysed with minimal or no preparation. The analysis can be carried out in a vacuum, after purging with helium, and at ambient atmospheric pressure. If smaller samples are required for analysis due to the size of the object or bulk sample, samples can be taken and crushed or pressed into pellets for analysis (Stuart, 2007:237). With the portable, hand held XRF analysers this is not usually necessary as they can be used to analyse different areas of the surface on large objects and samples.

In XRF analysis the objects or samples are exposed to a source of high energy photons produced by an X-ray source. When the X-ray photons interact with the materials being analysed they can be absorbed by the material and produce X-ray fluorescent radiation; transmitted through the material or scattered back, for example with Compton scattering and Raleigh scattering, depending on the thickness, density and composition of the material and the energy of the X-rays (Brouwer, 2010: 10-11). When sufficient energy is absorbed by the atoms in the material being analysed to overcome the binding energy, electrons are ejected from the inner K or L shells and vacancies in these shells are created. These vacancies destabilise the atoms and to regain stability, the vacancies in the inner shells are filled by the transfer of electrons from the outer shells such as the L or M shells. When this occurs a characteristic X-ray fluorescence is emitted as a result of the difference in energy between the two shells involved, where the outer shells have higher energy levels than the inner ones (Stuart, 2007: 234; Brouwer, 2010: 12). The difference in the energy between the shells is characteristic of the atoms in individual elements, and can be measured to indicate the elements present. This is illustrated in the diagram in **Figure 7,** provided in the product information for the Thermo Scientific Niton XL 3t portable XRF analyser used in the Research MSc.

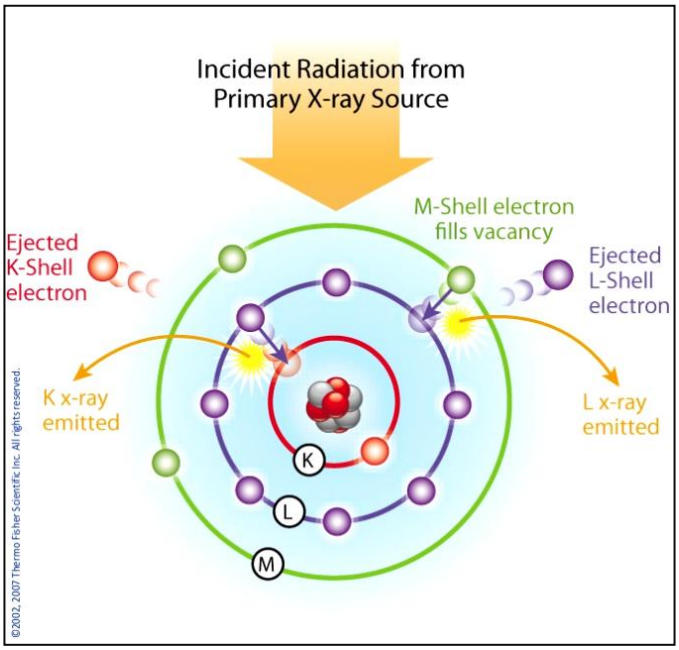


Figure 7: Diagram illustrating the transition of electrons involved in the emission of X-rays in XRF analysis (Thermo Scientific, 2011).

The difference in the energy levels is measured using an XRF spectrometer, which consists of an X-ray source and a detector system. The X-ray source is generally an X-ray tube, but can also be a radioactive source or synchrotron (Brouwer, 2010: 10). The two main types of detector systems are: wavelength dispersive X-ray fluorescence (WDXRF) and energy dispersive X-ray fluorescence (EDXRF). WDXRF spectrometers measure the wavelengths of the emitted X-ray radiation, using a Bragg crystal to reflect the different X-rays to the detector where they can be converted to a spectrum. EDXRF spectrometers measure the energy of the fluorescent radiation emitted directly from the material being analysed using semiconductor detectors, and do not require a Bragg reflector as the detector can separate the radiation from the material being tested into the radiation from the individual elements present (Brouwer, 2010: 21). The spectral resolution obtained with EDXRF spectrometers is considered to be inferior to that of the WDXRF spectrometers (Stuart, 2007: 236); however the EDXRF spectrometers have the advantage of being produced as portable, hand held analysers that are relatively inexpensive.

Recent developments in the technology of EDXRF analysers are thought to have improved their performance and in particular the accuracy and precision of the portable XRF equipment. For example, the development of the thermoelectrically cooled Geometrically Optimized Large Drift Detector (GOLDD) in the Thermo Scientific Niton XL 3t Series of portable XRF analysers is considered capable of analysing lighter elements such as Mg (atomic no. 12) and Al (atomic no. 13) without having to purge with helium or use vacuum pumps (Thermo Scientific, 2011). In addition there have been advances in the quantification methods with the use of fundamental parameters (FP), Compton normalization (CN) and spectral matching calibration based on internal reference libraries of 200 known alloys (Hurley, 2011; Thermo Scientific, 2011). The Thermo Scientific Niton XL 3t portable XRF analyser used in the Research MSc utilises an EDXRF detector system with these features. A diagram of the components in this pXRF analyser is shown in **Figure 8** and a photograph of the Thermo Scientific Niton XL 3t portable XRF analyser in the Science Faculty at the University of Lincoln and used in the Research MSc is shown in **Figure 9**.

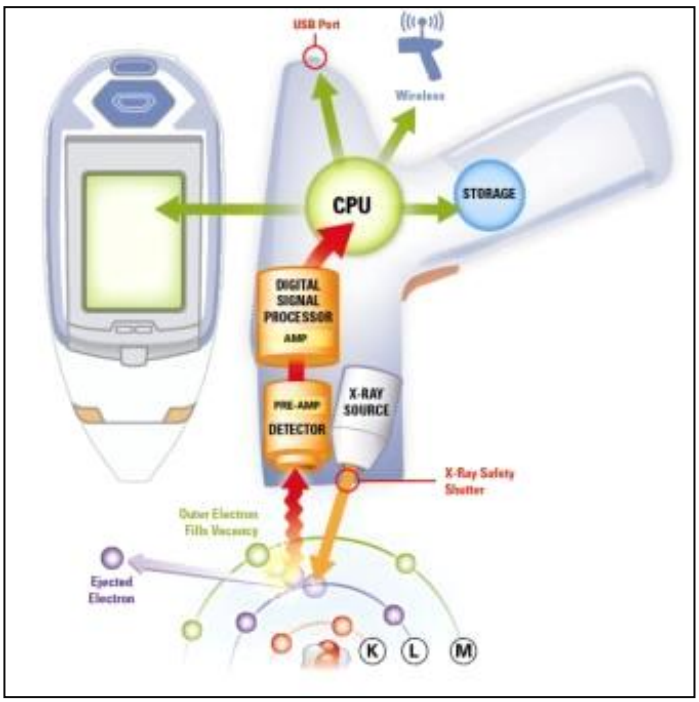


Figure 8: Diagram of the components in the Thermo Scientific Niton XL 3t portable XRF analyser (Thermo Scientific, 2011).

Figure 9: The Thermo Scientific Niton XL 3t portable XRF analyser secured in the laboratory bench top stand used in the Science Faculty at the University of Lincoln. The PC screen shows the connection to the pXRF analyser before it is operational.

3.4.2 Scanning Electron Microscopy – Energy Dispersive X-Ray Spectroscopy

Scanning electron microscopy (SEM) is an analytical technique that examines the topography or surface features of samples or objects at magnifications from 14 - 1 000 000x (FEI, 2013). When SEM is combined with energy dispersive X-ray spectroscopy (EDX) elemental analysis of samples or objects can be carried out (Stuart, 2007: 92). It can be a non-invasive technique if the objects or samples being analysed are secured on the stage in the sample chamber,

which is often c. 10 x 10 cm. Alternately small samples from objects can be mounted on aluminium SEM stubs with carbon tape or set in resin as cross sections for analysis. Cross sections can produce more reliable results as their surfaces are flat and can be more homogeneous than three-dimensional objects or samples. Taking samples from cultural heritage objects can be difficult, therefore the non-invasive application of SEM-EDX has advantages, however not all objects are suitable for analysing in the sample chamber due to their size and also because they may not be stable at high pressures. The use of variable pressure and environmental SEMs (VPSEM and ESEM) addresses this issue and facilitates the analysis of objects or samples at low vacuum and moderate pressure, without the need for applying conductive coatings (Stuart, 2007: 93). If the object or sample consists of non-conducting material it can be coated with a thin layer of a conductive material such as gold or carbon as part of the sample preparation.

In SEM-EDX analysis the sample or object is scanned with a beam of electrons to create an image of the surface. The electron beam is generated in a vacuum by an electron source, which consists of a tungsten filament, an anode and a Wehnelt cylinder (Stuart, 2007: 92). Electrons are released from the filament and accelerated towards the anode. As part of the electron beam passes through perforations in the anode an electromagnetic condenser lens focuses the beam towards the sample or object. When it reaches the surface of the object or sample it is swept back and forth over the selected area, which produces back-scattered electrons; secondary electrons; Auger electrons and X-ray fluorescence. The back-scattered electrons and secondary electrons generated are detected and amplified to produce the SEM images, while the X-ray fluorescence is measured by the EDX detector and indicates the elements present in the sample or object, since the X-ray energy is characteristic of individual elements (Stuart, 2007: 92-93). A schematic diagram of a scanning electron microscope is shown in **Figure 10** and a photograph of the FEI Inspect S50 environmental SEM-EDX in the Science Faculty at the University of Lincoln and used in the Research MSc is shown in **Figure 11**.

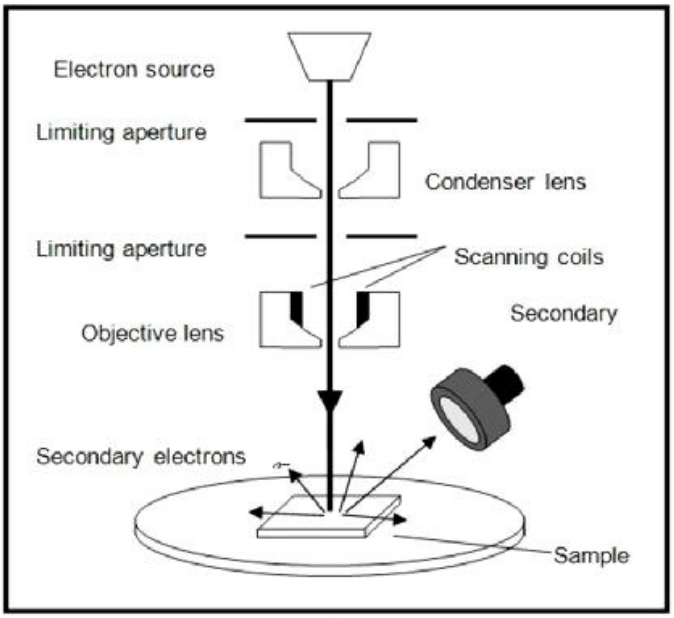


Figure 10: Schematic diagrams of a scanning electron microscope (SEM). (University of Warwick, Department of Physics, 2013)

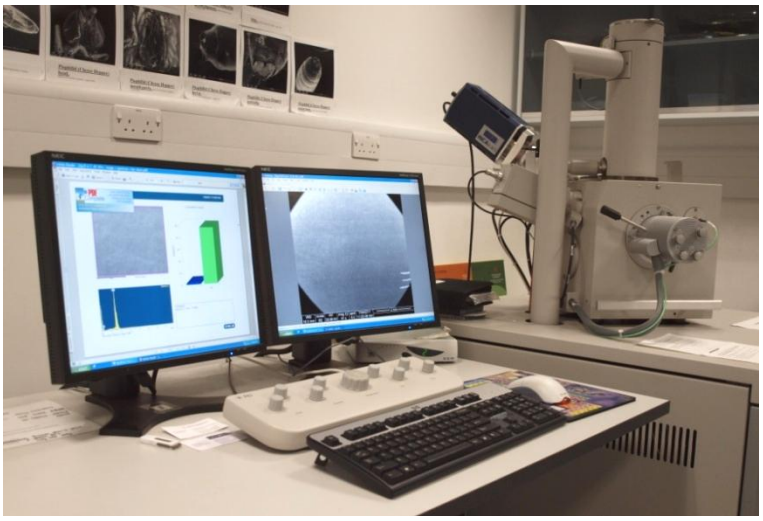


Figure 11: The FEI Inspect™ S50 environmental scanning electron microscope-energy dispersive X-ray spectrometer (ESEM-EDX) in the Science Faculty at the University of Lincoln.

The types of cultural heritage analysed with SEM-EDX or ESEM-EDX and VPSEM-EDX includes metals, inorganic pigments, stone, ceramics, glass, enamels, as well as textiles and a range of organic materials. The results of SEM-EDX are not generally quantitative unless calibration is carried out using reference standards; however it can provide detailed information on the morphology and microstructure of materials. It is particularly useful for examining the surface of objects or samples before and after treatments to assess the effects of the materials and methods used. Another application in conservation is to indicate the presence or absence of elements, such as chlorides in corrosion products, which can be unstable and require treatment. SEM-EDX analysis can also be used to map the distribution of elements over the

surface of samples or objects. The X-ray fluorescence emitted, which is characteristic of individual elements present, is measured relative to its position on the sample and variations in the intensity of the X-ray energy indicate the relative concentration of the elements (Materials Evaluation and Engineering, Inc., 2009: 1).

3.5 Experimental

3.5.1 Elemental Characterisation of the Metal Surfaces using Portable X-ray Fluorescence Spectroscopy

The pXRF analysis was carried out using a Thermo Scientific Niton XL 3t portable energy dispersive X-ray fluorescence (EDXRF/pXRF) analyser. It was secured in a stationary bench top Thermo Scientific Smart Stand for health and safety reasons, as well as to increase the physical stability of the pXRF analyser, as this is considered important for providing reliable results (Goodale et al., 2012: 879). The pXRF analyser was connected to a PC with Niton Data Transfer (NDT) software for remote operation and downloading the results. An integrated colour CCD camera incorporated into the Thermo Scientific Niton XL 3t pXRF analyser, also operated remotely with the Niton software, was used to locate and record images of the analysis sites on each of the medals. The Thermo Scientific Niton XL 3t pXRF is shown in **Figure 12.**

Figure 12: The Thermo Scientific Niton XL 3t pXRF analyser secured in the bench top Thermo Scientific Smart Stand and connected to the PC with the Niton Data Transfer (NDT) software. The lid is open, showing the inside of the sample chamber with the 8 mm circular opening of the pXRF analyser, adjacent to the orange strip in the centre of the horizontal surface. The PC screen shows the connection to the pXRF analyser before it is operational.

The Niton XL 3t pXRF analyser utilises a thermoelectrically cooled Geometrically Optimized Large Drift Detector (GOLDD), which is considered capable of analysing lighter elements from Mg (atomic no. 12) and Al (atomic no. 13) without purging with helium or the use of vacuum pumps, up to heavier elements such as U (atomic no. 92) (Thermo Scientific, 2011). The resolution of the detector is < 185 eV at 60 000 cps and 4 µsec shaping time, with over 180 000 detector events recorded per second and 80 MHz digital signal processing. Low, main and light element filters were used for the detection of the above range of elements in the Alloy mode. The X-ray tube consists of a gold anode operating at 9-50 kV voltage and 0-40 µA current. The analyses were carried out in an air-path with a spot size of 8 mm; a measurement time of 60 seconds and an analysis depth of 10 µm (Hurley, 2011; Barrett, 2013; Thermo Scientific, 2013). The quantification method for the Niton XL 3t pXRF analyser is a fundamental parameters based analysis integrated with a matrix recognition algorithm, and there is an internal reference library of hundreds of standards that corrects and calibrates the pXRF analyser (Thermo Scientific, 2008a and 2013). This type of quantification method, as well as the use of a silicon drift detector or SDD were found to produce accurate results in the recent inter-laboratory evaluation of the XRF analysis of historic copper alloys (Heginbotham et al., 2011: 252). The estimated optimal limits of detection (LODs) provided in the product specifications for the Thermo Scientific Niton XL 3t Series pXRF analysers are listed in **Table 1**, and this includes elements in copper, iron and aluminium based alloys (Thermo Scientific, 2008a and 2008b; Barrett, 2013).

Table 1: Estimated optimal limits of detection (LODs) for the Thermo Scientific Niton XL 3t Series pXRF analysers. (Thermo Scientific XL 3t Series XRF Analyzer, Product Specifications, 2008a and 2008b; Barrett, 2013). NA denotes not applicable.

	Matrix (conc.)		
Element	**Cu Base wt. % 60 s per filter**	**Fe Base wt. % 60 s per filter**	**Al Base wt. % 60 s per filter**
Zn	0.030	0.005	0.010
Cu	NA	0.009	0.030
Ni	0.011	0.020	0.010
Al	0.700	0.500	NA
Cr	0.005	0.003	0.015
Ti	0.003	0.003	0.010
Si	0.080	0.075	0.150
Mg	NA	NA	0.650
Sn	0.015	0.008	-
Sb	0.008	0.006	-
Co	0.005	0.080	-
Mo	0.002	0002	-
Nb	0.003	0.002	-
Mn	0.007	0.020	-

Given the limitations involved in the pXRF analysis of plated, patinated, heat-treated, tarnished or corroded metal objects, the central area of each of the 60 medals was analysed, where the high points on the surface are worn and areas of the base metal are exposed (van Langh et al., 2011; Smith, 2011; Goodale et al., 2012). This was also intended to minimise any inconsistencies in the instrument-sample distance when using an air-path pXRF analyser (Craig et al., 2007, McGlinchey and Trentelman, 2008). The pXRF analysis was non-invasive therefore the 60 medals were analysed without surface preparation or cleaning. Final adjustments to the location of the pXRF analysis site on each medal were made using the integrated colour CCD camera image to ensure that an area with some exposed base metal was analysed, in particular the medals identified with plated, tarnished or corroded surfaces in the microscopic examination. The placement of the medals over the 8 mm opening in the pXRF analyser is shown in **Figure 13.**

Figure 13: Medal 54 placed over the 8mm opening in the Niton XL 3t pXRF analyser. The PC screen shows the connection to the pXRF analyser before it is operational.

Both sides of the 60 religious medals were analysed in triplicate giving a weight % (wt. %) for the elements detected and an error value. Niton pXRF analysers provide a two-sigma precision value for each element, which represents an error of two standard deviations (2s) on either side of the reading, giving a confidence interval of approximately 95 % for the results, which is the American Society for Testing and Materials or ASTM industry standard (Thermo Scientific,

2008a). This experimental procedure was repeated on the 60 medals to check the reproducibility of the first set of pXRF results, as well as to increase the data base on which the conclusions about the types of alloys used in the religious medals could be made. In the first set of data, the calibration of the pXRF analyser was regularly checked against a number of metal reference standards over a period of approximately one month including silver, copper, zinc, iron and brass alloys of known compositions, as well as the certified metal calibration disc provided with the Niton XL 3t XRF analyser. The pXRF results for the copper, silver, zinc and brass reference standards are shown in **Table 2**, with error factors based on 2s. In the second set of data for the 60 medals obtained over the following month, the results of the regular internal calibration of the pXRF analyser using the integrated reference library were recorded and the results are shown in **Table 3**.

Table 2: pXRF analysis of the copper, silver, zinc and brass reference standards supplied by Goodfellow Cambridge Ltd., U.K., where S.D. denotes standard deviation (s).

Reference Standard		**Copper 99.95 wt. %**		**Silver 99.9 wt. %**		**Zinc 99.99 wt. %**		**Brass Cu 63 wt. %**		**Zn 37 wt. %**	
Reading #		**Cu wt. %**	**± Cu Error**	**Ag wt. %**	**± Ag Error**	**Zn wt. %**	**± Zn Error**	**Cu wt. %**	**± Cu Error**	**Zn wt. %**	**± Zn Error**
	1	99.7	0.41	98.8	0.54	99.4	0.89	63.8	0.32	35.9	0.21
	2	99.7	0.42	99.2	0.53	99.4	0.87	63.7	0.31	35.9	0.20
	3	99.7	0.42	99.1	0.54	99.4	0.86	63.7	0.31	36.0	0.20
	4	99.6	0.42	99.1	0.53	99.3	0.87	63.6	0.33	35.8	0.21
	5	99.7	0.39	99.1	0.55	99.2	0.86	63.7	0.32	35.9	0.20
	6	99.7	0.39	99.1	0.53	99.2	0.86	63.7	0.33	35.9	0.21
	7	-	-	99.2	0.22	99.7	0.77	-	-	-	-
	8	-	-	99.3	0.22	99.7	0.77	-	-	-	-
	9	-	-	99.3	0.22	99.7	0.75	-	-	-	-
Mean		99.7		99.1		99.4		63.7		35.9	
S.D. (s)		0.04		0.14		0.22		0.064		0.065	
2s/Error		± 0.08		± 0.28		± 0.44		± 0.13		± 0.13	

Table 3: Results of the regular integrated calibration of the Niton XL 3t pXRF analyser.

Calibrated pXRF Analyser			**≤ 60 sec**			**< 180 Ek**	**7.17 ± 0.1**
Reading #		**Type**	**Duration**	**Units**	**Sigma Value**	**Res**	**EScale**
	1	ShutterCal	58.0	cps	2	173.8	7.18
	2	ShutterCal	60.0	cps	2	173.2	7.17
	3	ShutterCal	58.1	cps	2	165.5	7.17
	4	ShutterCal	60.0	cps	2	170.9	7.17
	5	ShutterCal	57.9	cps	2	174.1	7.17
	6	ShutterCal	58.0	cps	2	176.3	7.17
	7	ShutterCal	58.1	cps	2	177.5	7.18
	8	ShutterCal	58.1	cps	2	168.8	7.17
	9	ShutterCal	58.0	cps	2	176.5	7.17

Additional reproducibility tests were carried out and consisted of analysing medals 1-5 consecutively, on one side with three readings per medal. This was repeated five times to give a total of 15 readings for each of the five medals. The pXRF results for the 15 repeats of medals 1-5 are shown in **Table 4** and include the mean, standard deviation and error factors based on 2s, as well as the total measurement errors. The total measurement errors were calculated by combining the standard deviation (s) of the 15 readings with the counting error (C.E.) for each element according to equation (1) (Colston, 2013). The maximum total measurement error for each of the elements is included in Table 4.

Total Measurement Error = $\sqrt{(\sum s^2 + \overline{C.E.^2})}$ (1)

Table 4: Reproducibility tests for medals 1-5 with errors based on 2 standard deviations (2s), as well as the maximum total measurement error for the individual elements. The wt. % values are the mean of the three pXRF readings for the five repeats for each medal. * denotes medals with silver plating, as indicated by the pXRF results combined with stereo microscopic examination and the ESEM-EDX mapping. n.d. denotes not detected.

Medals	Elements wt. % ± Total Measurement Error							
	Cu ± 1.48	**Zn ± 0.51**	**Ni ± 0.32**	**Ag ± 1.33**	**Al ± 1.47**	**Fe ± 0.11**	**Pb ± 0.05**	**Sn ± 0.04**
JCm1s1-1	98.5	n.d.	n.d.	n.d.	n.d.	0.29	0.14	n.d.
JCm1s1-2	98.3	n.d.	n.d.	n.d.	n.d.	0.26	0.13	n.d.
JCm1s1-3	98.4	n.d.	n.d.	n.d.	n.d.	0.30	0.14	n.d.
JCm1s1-4	98.7	n.d.	n.d.	n.d.	n.d.	0.24	0.13	n.d.
JCm1s1-5	98.7	n.d.	n.d.	n.d.	n.d.	0.26	0.14	n.d.
S.D. (s)	0.17					0.026	0.01	
Mean	98.5					0.270	0.14	
2s/Error	0.34					0.052	0.02	
JCm2s1-1 *	50.1	17.3	0.041	28.0	n.d.	0.11	0.32	n.d.
JCm2s1-2 *	51.0	17.8	0.040	27.6	n.d.	0.11	0.34	n.d.
JCm2s1-3 *	48.6	17.5	n.d.	30.6	n.d.	0.10	0.33	n.d.
JCm2s1-4 *	49.4	16.9	0.049	28.0	n.d.	0.11	0.29	n.d.
JCm2s1-5 *	48.2	16.9	0.036	30.0	n.d.	0.10	0.29	n.d.
S.D. (s)	1.16	0.38	0.005	1.37		0.004	0.02	
Mean	49.5	17.3	0.042	28.8		0.10	0.31	
2s/Error	2.32	0.760	0.010	2.74		0.01	0.04	
JCm3s1-1	0.076	0.36	n.d.	n.d.	95.5	1.43	0.020	n.d.
JCm3s1-2	0.077	0.34	n.d.	n.d.	96.0	1.34	0.018	n.d.
JCm3s1-3	0.071	0.35	n.d.	n.d.	95.7	1.38	0.018	n.d.
JCm3s1-4	0.070	0.31	n.d.	n.d.	94.2	1.25	0.017	n.d.
JCm3s1-5	0.077	0.35	n.d.	n.d.	96.1	1.35	0.019	n.d.
S.D. (s)	0.003	0.019			0.770	0.07	0.001	
Mean	0.074	0.34			95.5	1.35	0.018	
2s/Error	0.01	0.04			1.54	0.13	0.002	
JCm4s1-1 *	81.6	12.2	0.15	4.69	n.d.	0.51	0.51	0.11
JCm4s1-2 *	81.4	12.0	0.16	4.73	n.d.	0.52	0.52	0.11
JCm4s1-3 *	82.1	12.0	0.16	4.51	n.d.	0.53	0.53	0.15
JCm4s1-4 *	81.2	12.1	0.15	5.27	n.d.	0.54	0.54	0.15
JCm4s1-5 *	82.0	11.9	0.15	4.55	n.d.	0.56	0.56	0.12
S.D. (s)	0.41	0.12	0.005	0.30		0.017	0.017	0.019
Mean	81.7	12.1	0.15	4.75		0.53	0.53	0.13
2s/Error	0.810	0.24	0.01	0.60		0.035	0.035	0.04

Table 4 continued: Reproducibility tests for medals 1-5 with errors based on 2 standard deviations (2s), as well as the maximum total measurement error for the individual elements. The wt. % values are the mean of the three pXRF readings for the five repeats for each medal. * denotes medals with silver plating, as indicated by the pXRF results combined with stereo microscopic examination and the ESEM-EDX mapping. n.d. denotes not detected.

Medals	**Elements wt. % ± Total Measurement Error**							
	Cu ± 1.48	**Zn ± 0.51**	**Ni ± 0.32**	**Ag ± 1.33**	**Al ± 1.47**	**Fe ± 0.11**	**Pb ± 0.05**	**Sn ± 0.04**
JCm5s1-1 *	42.3	16.4	8.35	21.1	n.d.	0.33	0.33	n.d.
JCm5s1-2 *	43.7	16.9	8.64	21.1	n.d.	0.31	0.31	n.d.
JCm5s1-3 *	40.4	15.9	7.96	21.2	1.98	0.40	0.40	n.d.
JCm5s1-4 *	44.3	17.2	8.77	20.9	n.d.	0.26	0.26	n.d.
JCm5s1-5 *	43.4	16.7	8.61	20.0	n.d.	0.32	0.32	n.d.
S.D. (s)	1.52	0.50	0.32	0.50	n.d.	0.05	0.05	
Mean	42.8	16.6	8.47	20.9		0.32	0.32	
2s/Error	3.03	1.01	0.64	1.01		0.10	0.10	

3.5.2 Elemental Mapping of Plated and Corroded Metal Surfaces using Scanning Electron Microscopy coupled with Energy Dispersive X-Ray Spectroscopy

Medals that were tarnished, corroded or appeared to have been plated or coated were identified during the stereo microscopic examination. Of those identified, medals 2, 10, 13, 16, 26, 27, 38, 41, 42, 43, 53 and 54 were analysed using a tungsten based FEI Inspect S50 environmental scanning electron microscope coupled with an energy dispersive X-ray spectrometer (ESEM-EDX) in the Science Faculty at the University of Lincoln to examine the silver plating and surface deposits. The FEI Inspect S50 ESEM-EDX analyses non-conductive and conductive samples in high and low vacuum, with a magnification range of 13 to 1 000 000x, an accelerating voltage of 200V-30 kV and a continuously adjustable probe current of up to 2 µA (FEI, 2013). The software used was Oxford INCA x-act EDX xT Microscope Server. ESEM-EDX mapping was carried out to complement the pXRF analyses since there can be limitations with the XRF technique on inhomogeneous samples. In addition the surfaces of many of the religious medals are worn and the ESEM-EDX mapping was used to examine traces of silver plating remaining and thin layers of tarnish or corrosion. The medals were secured to aluminium SEM stubs with carbon tape and placed on the circular stage in the ESEM-EDX chamber for analysis under high vacuum at magnifications from 40-150x with the following operating parameters: 15-20 kV, a spot size of 6.0, a working distance of c.10 mm and an acquisition time of 60 seconds.

3.6 Results and Discussion

3.6.1 Elemental Characterisation of the Metal Surface using pXRF

The results of the pXRF analysis for the 60 modern religious medals in the first and second sets of data are consistent, indicating instrument stability and precision, which is in line with previous pXRF studies (Craig, et al., 2007, Goodale, et al., 2012). A range of elements from Al to Pb were detected in the 60 medals, with the main major and minor elements identified as copper (Cu), zinc (Zn), nickel (Ni), silver (Ag), aluminium (Al), iron (Fe), lead (Pb) and tin (Sn). A comparison of the pXRF results in the two sets of data for Cu, Zn, Ni and Ag in medals 1-17, i.e. the first stylistic group of the religious medals is shown in the scatter plots in **Figures 14-17**, illustrating the consistency in the data.

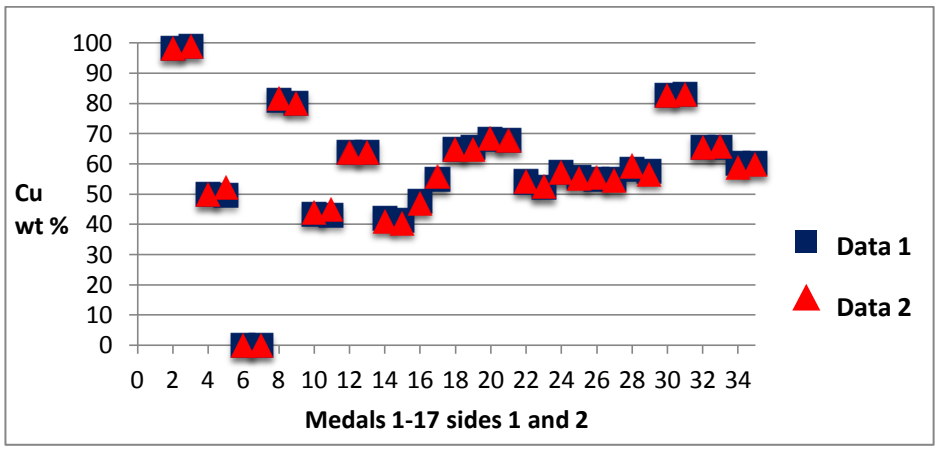


Figure 14: Scatter plot of the pXRF results for copper in medals 1-17 sides 1 and 2, with the first set of data in blue and the second in red.

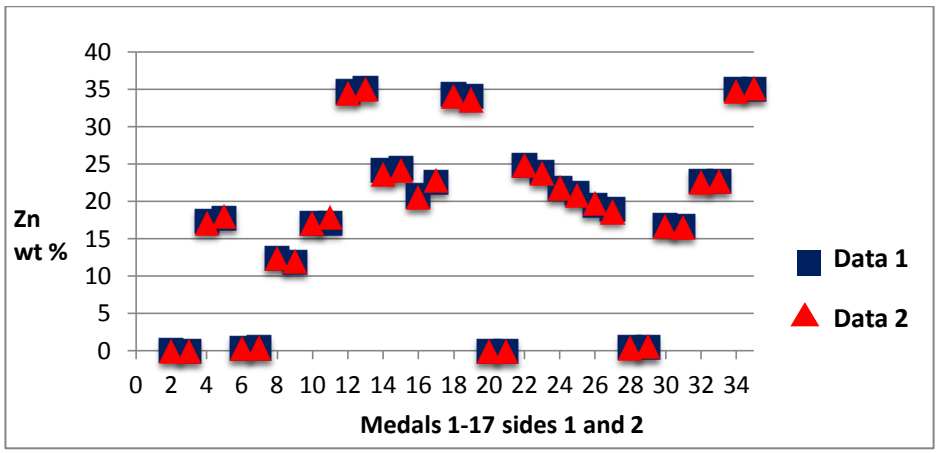


Figure 15: Scatter plot of the pXRF results for zinc in medals 1-17 sides 1 and 2, with the first set of data in blue and the second in red.

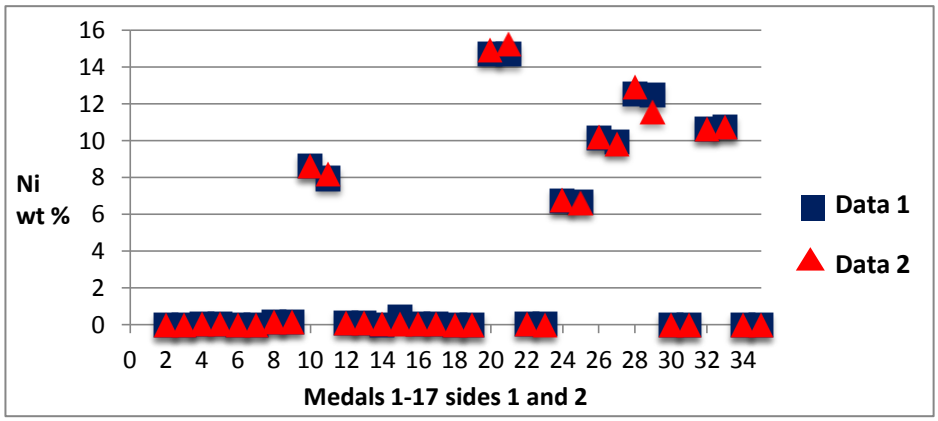


Figure 16: Scatter plot of the pXRF results for nickel in medals 1-17 sides 1 and 2, with the first set of data in blue and the second in red.

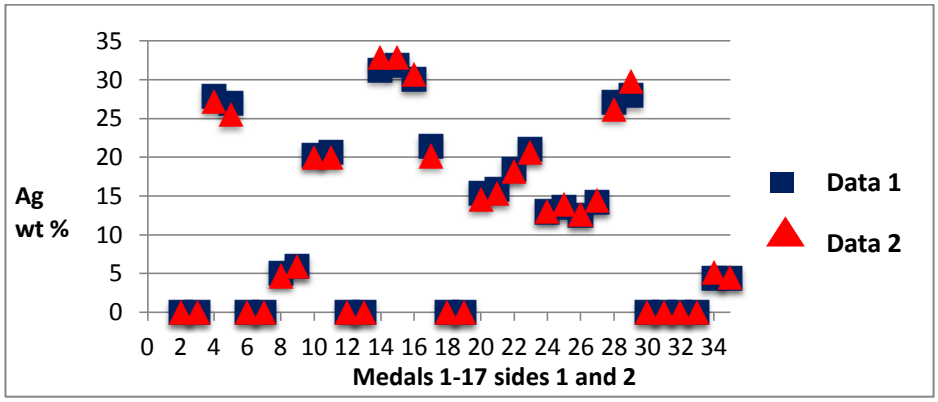


Figure 17: Scatter plot of the pXRF results for silver in medals 1-17 sides 1 and 2, with the first set of data in blue and the second in red.

As evident in the scatter plots in Figures 14-17, there were differences in the pXRF results for the two sides on some medals, particularly with the Ag wt. %. This appears to be due to the worn condition of many of the medals, particularly on the back surfaces and the inhomogeneous nature of the silver plated, tarnished or corroded surfaces on some of the medals.

The mean wt. % of the six readings for the major and minor elements on both sides of medals 1-60 are shown in **Table 5**, with 2s error factors, as well as the maximum total measurement errors for the individual elements based on the reproducibility tests. The medals identified with silver plating by the pXRF analysis combined with the stereo microscopic examination and the ESEM-EDX mapping are denoted with an '*' symbol; several medals with worn surfaces that appear to have once had silver plating are denoted with '*w' and medals with worn surfaces that may have once had silver plating but require further analysis to confirm this are denoted with 'w'. The following abbreviations for the different types of religious medals are

also used in Table 5: JC – Jesus Christ medals ; IOP – Infant of Prague medals ; MC – Madonna and Child medals ; BS – Blessed Sacrament medals and D – Diverse medals.

Table 5: pXRF results for medals 1-60 sides 1 and 2 divided into their types. The wt. % values are the mean of the first and second sets of data, with an error factor 2 standard deviations (2s), as well as the maximum total measurement error for the individual elements based on the reproducibility tests for medals 1-5. n.d. denotes not detected.

Medals	Elements wt. % ± Total Measurement Error							
	Cu ± 1.48	**Zn ± 0.51**	**Ni ± 0.32**	**Ag ± 1.33**	**Al ± 1.47**	**Fe ± 0.11**	**Pb ± 0.05**	**Sn ± 0.04**
JCm1s1	98.3 ± 0.07	0.097 ± 0.05	n.d.	n.d.	n.d.	0.280 ± 0.01	0.141 ± 0.01	n.d.
JCm1s2	98.9 ± 0.09	n.d.	n.d.	n.d.	n.d.	0.317 ±0.02	0.119 ± 0.002	n.d.
JCm2s1 *	49.9 ± 0.10	17.3 ± 0.37	0.046 ± 0.01	27.5 ±0.78	n.d.	0.093 ± 0.02	0.303 ± 0.03	n.d.
JCm2s2 *	51.0 ± 3.83	17.9 ± 0.44	0.040 ± 0.01	26.2 ± 2.15	n.d.	0.108 ± 0.01	0.285 ± 0.04	n.d.
JCm3s1	0.10 ± 0.01	0.30 ± 0.001	n.d.	n.d.	95.9 ± 0.12	1.33 ± 0.01	0.018 ± 0.001	n.d.
JCm3s2	0.10 ±0.004	0.40 ± 0.01	n.d.	n.d.	94.9 ± 0.77	1.48 ± 0.04	0.022 ± 0.001	n.d.
JCm4s1 *	81.3 ± 0.81	12.4 ± 0.03	0.149 ±0.003	4.83 ± 0.37	n.d.	0.028 ± 0.001	0.542 ± 0.02	0.092 ± 0.02
JCm4s2 *	80.2 ± 0.11	11.9 ± 0.10	0.151 ± 0.01	5.90 ± 0.06	n.d.	0.027 ± 0.01	0.486 ± 0.02	0.083 ± 0.04
JCm5s1 *	43.7 ± 1.24	17.0 ± 0.08	8.64 ± 0.03	20.2 ± 0.35	n.d.	0.065 ± 0.02	0.290 ± 0.003	n.d.
JCm5s2 *	44.1 ± 2.90	17.5 ± 1.13	8.09 ± 0.38	20.3 ± 0.73	2.02 ± 1.00	0.045 ± 0.03	0.293 ± 0.06	n.d.
JCm6s1 w	63.9 ± 0.01	34.5 ± 0.29	0.096 ±0.004	n.d.	n.d.	0.054 ± 0.003	0.358 ± 0.02	n.d.
JCm6s2 w	63.9 ± 0.21	35.0 ± 0.18	0.095 ± 0.01	n.d.	n.d.	0.054 ± 0.01	0.379 ± 0.01	n.d.
JCm7s1 *	41.5 ±1.36	23.9 ± 0.63	n.d.	32.1 ± 2.25	n.d.	0.081 ± 0.01	0.551 ± 0.01	n.d.
JCm7s2 *	40.9 ± 1.07	24.3 ± 0.46	0.240 ± 0.52	32.0 ±1.41	n.d.	0.098 ± 0.04	0.510 ± 0.05	n.d.
JCm8s1 *	47.3 ± 0.77	20.6 ± 0.21	0.062 ±0.003	30.3 ± 0.89	n.d.	0.084 ± 0.02	0.246 ± 0.06	n.d.
JCm8s2 *	55.3 ± 1.41	22.7 ± 0.49	0.065 ±0.001	20.8 ± 1.61	n.d.	0.096 ± 0.01	0.284 ± 0.01	n.d.
JCm9s1 w	64.8 ± 0.13	34.2 ± 0.46	n.d.	n.d.	n.d.	0.027 ± 0.003	0.043 ± 0.003	n.d.
JCm9s2 w	65.5 ± 0.71	33.9 ± 0.72	n.d.	n.d.	n.d.	0.026 ± 0.01	0.039 ± 0.01	n.d.
JCm10s1 *	68.4 ± 0.46	n.d.	14.8 ± 0.30	15.0 ± 1.05	n.d.	0.027 ± 0.01	0.020 ± 0.004	n.d.
JCm10s2 *	67.7 ± 0.10	n.d.	15.0 ± 0.76	15.6 ± 0.75	n.d.	0.030 ± 0.02	0.021 ± 0.001	n.d.

Table 5 continued: pXRF results for medals 1-60 sides 1 and 2 divided into their types. The wt. % values are the mean of the first and second sets of data, with an error factor 2 standard deviations (2s), as well as the maximum total measurement error for the individual elements based on the reproducibility tests for medals 1-5. n.d. denotes not detected.

Medals	Elements wt. % ± Total Measurement Error							
	Cu ± 1.48	**Zn ± 0.51**	**Ni ± 0.32**	**Ag ± 1.33**	**Al ± 1.47**	**Fe ± 0.11**	**Pb ± 0.05**	**Sn ± 0.04**
JCm11s1 *	54.2 ± 0.35	24.8 ± 0.02	0.034 ±0.004	18.3 ± 0.27	n.d.	0.059 ± 0.003	0.558 ± 0.03	n.d.
JCm11s2 *	52.3 ± 0.36	23.9 ± 0.11	0.037 ± 0.02	20.8 ± 0.53	n.d.	0.061 ± 0.01	0.523 ± 0.03	n.d.
JCm12s1 *	57.1 ± 0.21	21.8 ± 0.06	6.74 ± 0.04	13.0 ± 0.06	n.d.	0.072 ± 0.01	0.049 ± 0.001	n.d.
JCm12s2 *	55.5 ± 0.43	21.9 ± 0.30	6.65 ± 0.09	13.8 ± 0.45	n.d.	0.091 ± 0.01	0.053 ± 0.02	n.d.
JCm13s1 *	55.3 ± 0.87	19.6 ± 0.29	10.2 ± 0.03	12.6 ± 0.25	n.d.	0.162 ± 0.01	0.114 ± 0.003	n.d.
JCm13s2 *	54.5 ± 0.48	18.8 ± 0.52	9.90 ± 0.18	14.3 ± 0.42	n.d.	0.146 ± 0.003	0.111 ± 0.02	n.d.
JCm14s1 *	58.7 ± 1.70	0.50 ± 0.10	12.7 ± 0.55	26.7 ± 1.25	n.d.	0.041 ± 0.01	0.080 ± 0.01	n.d.
JCm14s2 *	57.1 ± 1.51	0.50 ± 0.07	12.4 ± 1.27	28.9 ± 2.55	n.d.	0.035 ± 0.01	0.082 ± 0.001	n.d.
JCm15s1 w	82.8 ± 0.05	16.7 ± 0.17	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
JCm15s2 w	83.0 ± 0.14	16.6 ± 0.22	n.d.	n.d.	n.d.	0.020 ± 0.01	n.d.	n.d.
JCm16s1 *w	65.5 ± 0.23	22.6 ± 0.29	10.7 ± 0.01	n.d.	n.d.	0.109 ± 0.001	0.130 ± 0.004	n.d.
JCm16s2 *w	65.6 ± 0.27	22.7 ± 0.09	10.8 ± 0.04	n.d.	n.d.	0.114 ± 0.001	0.130 ± 0.003	n.d.
JCm17s1 *	59.5 ± 1.45	34.9 ± 0.41	n.d.	4.75 ± 1.07	n.d.	n.d.	n.d.	n.d.
JCm17s2 *	59.9 ± 0.74	35.1 ± 0.08	n.d.	4.50 ± 0.32	n.d.	n.d.	n.d.	n.d.
IOPm18s1 w	61.4 ± 0.13	36.7 ± 0.14	n.d.	n.d.	n.d.	0.065 ± 0.01	0.349 ± 0.02	n.d.
IOPm18s2 w	61.8 ± 0.19	36.5 ± 0.05	n.d.	n.d.	n.d.	0.055 ± 0.002	0.352 ± 0.01	n.d.
IOPm19s1 *	52.9 ± 0.48	28.0 ± 0.1	n.d.	17.8 ± 0.09	n.d.	n.d.	n.d.	n.d.
IOPm19s2 *	60.1 ± 1.9	30.2 ± 0.37	n.d.	8.56 ± 1.98	n.d.	n.d.	n.d.	n.d.
IOPm20s1 *	52.2 ± 3.97	27.8 ± 0.11	n.d.	17.6 ± 4.94	n.d.	0.076 ± 0001	0.021 ± 0.003	n.d.
IOPM20s2 *	57.0 ± 0.13	29.3 ± 0.15	n.d.	11.9 ± 0.66	n.d.	0.040 ± 0004	0.023 ± 0.01	n.d.

Table 5 continued: pXRF results for medals 1-60 sides 1 and 2 divided into their types. The wt. % values are the mean of the first and second sets of data, with an error factor 2 standard deviations (2s), as well as the maximum total measurement error for the individual elements based on the reproducibility tests for medals 1-5. n.d. denotes not detected.

Medals	Elements wt. % ± Total Measurement Error							
	Cu ± 1.48	**Zn ± 0.51**	**Ni ± 0.32**	**Ag ± 1.33**	**Al ± 1.47**	**Fe ± 0.11**	**Pb ± 0.05**	**Sn ± 0.04**
IOPm21s1 *	60.7 ± 0.63	20.3 ± 0.27	8.34 ± 0.09	9.28 ± 0.20	n.d.	0.028 ± 0.003	0.007 ± 0.02	n.d.
IOPm21s2 *	60.9 ± 0.27	20.7 ± 0.12	8.38 ± 0.05	8.89 ± 0.19	n.d.	0.032 ± 0.001	0.018 ± 0.003	n.d.
IOPm22s1 w	83.6 ± 0.38	15.7 ± 0.06	n.d.	n.d.	n.d.	0.021 ± 0.001	n.d.	n.d.
IOPm22s2 w	83.9 ± 0.03	15.2 ± 0.24	n.d.	n.d.	n.d.	0.040 ± 0.01	n.d.	n.d.
IOPm23s1*w	67.2 ± 0.14	31.4 ± 0.03	0.02 ±0.003	n.d.	n.d.	0.067 ± 0.01	0.232 ± 0.02	0.045 ± 0.004
IOPm23s2*w	67.4 ± 0.68	30.0 ± 0.33	0.02 ±0.001	n.d.	1.99 ± 0.93	0.072 ± 0.004	0.206 ± 0.003	0.044 ± 0.013
MCm24s1 *	64.2 ± 0.17	31.4 ± 0.02	n.d.	3.43 ± 0.11	n.d.	0.028 ± 0.003	0.014 ± 0.004	n.d.
MCm24s2 *	63.9 ± 0.45	31.8 ± 0.02	n.d.	1.45 ± 4.11	n.d.	0.039 ± 0.01	0.015 ± 0.001	n.d.
MCm25s1 *	63.2 ± 0.60	30.8 ± 0.06	0.03 ± 0.01	5.06 ± 0.57	n.d.	0.027 ± 0.01	0.029 ± 0.001	n.d.
MCm25s2 *	62.3 ± 1.16	30.7 ± 0.03	0.03 ±0.003	5.69 ± 1.00	n.d.	n.d.	0.030 ± 0.004	n.d.
MCm26s1 *	83.6 ± 0.04	9.42 ± 0.19	n.d.	4.04 ± 0.19	n.d.	0.052 ± 0.01	0.041 ± 0.01	n.d.
MCm26s2 *	85.0 ± 1.25	9.44 ± 0.14	n.d.	3.52 ± 0.59	n.d.	0.043 ± 0.01	0.023 ± 0.01	n.d.
MCm27s1*w	65.0 ± 0.39	23.1 ± 0.25	10.2 ± 0.10	n.d.	n.d.	0.054 ± 0,01	0.085 ± 0.004	n.d.
MCm27s2*w	65.5 ± 0.24	23.4 ± 0.02	10.3 ± 0.03	n.d.	n.d.	0.054 ± 0.01	0.084 ± 0.003	n.d.
MCm28s1	73.3 ± 0.09	n.d.	23.7 ± 0.05	n.d.	n.d.	0.113 ± 0.01	n.d.	n.d.
MCm28s2	73.9 ± 0.58	n.d.	24.5 ± 0.23	n.d.	n.d.	0.115 ± 0.004	n.d.	n.d.
MCm29s1 *	64.9 ± 0.06	20.6 ± 0.04	6.87 ± 0.06	6.46 ± 0.08	n.d.	0.161 ± 0.02	0.036 ± 0.001	n.d.
MCm29s2 *	64.4 ± 1.17	20.1 ± 0.37	6.64 ± 0.23	6.84 ± 0.39	n.d.	0.172 ± 0.05	0.046 ± 0.001	n.d.
MCm30s1 *	58.6 ± 1.67	16.2 ± 0.78	13.4 ± 0.67	10.4 ± 3.85	n.d.	0.078 ± 0.00	0.077 ± 0.004	n.d.
MCm30s2 *	56.4 ± 2.03	15.4 ± 0.63	12.9 ± 0.72	13.4 ± 4.32	n.d.	0.070 ± 0.003	0.081 ± 0.001	n.d.

Table 5 continued: pXRF results for medals 1-60 sides 1 and 2 divided into their types. The wt. % values are the mean of the first and second sets of data, with an error factor 2 standard deviations (2s), as well as the maximum total measurement error for the individual elements based on the reproducibility tests for medals 1-5. n.d. denotes not detected.

Medals	Elements wt. % ± Total Measurement Error							
	Cu ± 1.48	**Zn ± 0.51**	**Ni ± 0.32**	**Ag ± 1.33**	**Al ± 1.47**	**Fe ± 0.11**	**Pb ± 0.05**	**Sn ± 0.04**
MCm31s1	0.055 ± 0.00	0.094 ± 0.01	0.159 ± 0.00	n.d.	95.8 ± 0.59	1.66 ± 0.04	0.004 ± 0.00	n.d.
MCm31s2	0.046 ± 0.00	0.083 ± 0.01	0.156 ± 0.02	n.d.	96.2 ± 0.61	1.56 ± 0.13	0.003 ± 0.003	n.d.
MCm32s1*w	66.5 ± 0.34	32.8 ± 0.04	n.d.	n.d.	n.d	0.025 ± 0.01	0.015 ± 0.01	n.d.
MCm32s2*w	65.5 ± 0.02	32.5 ± 0.03	n.d.	n.d.	n.d	0.024 ± 0.01	0.015 ± 0.00	n.d.
MCm33s1*w	95.0 ± 0.34	n.d.	n.d.	n.d.	n.d	n.d	n.d.	0.067 ± 0.03
MCm33s2*w	93.8 ± 0.38	n.d.	n.d.	n.d.	n.d	n.d.	n.d.	0.041 ± 0.11
BSm34s1	0.006 ±0.004	0.037 ± 0.004	n.d.	n.d.	98.1 ± 1.11	0.522 ± 005	0.003 ± 0.001	n.d
BSm34s2	0.005 ± 0.00	0.039 ± 0.001	n.d.	n.d.	98.0 ± 0.53	0.543 ± 0.05	0.002 ± 0.001	n.d
BSm35s1	90.7 ± 0.39	n.d.	n.d.	n.d.	n.d	n.d.	0.053 ± 0.003	0.012 +/- 0.03
BSm35s2	90.1 ± 0.96	n.d.	n.d.	n.d.	n.d	n.d.	0.052 ± 0.01	n.d.
BSm36s1	0.022 ± 0.01	0.022 ± 0.01	n.d.	n.d.	91.4 ± 6.15	0.540 ± 003	0.004 ± 0.00	n.d.
BSm36s2	0.027 ±0.004	0.025 ± 0.00	n.d.	n.d.	92.7 ± 1.88	0.556 ± 0.02	0.004 ± 0.001	n.d.
BSm37s1	0.019 ± 0.00	0.026 ± 0.001	n.d.	n.d.	96.1 ± 0.47	0.695 ± 0.02	0.006 ± 0.00	n.d.
BSm37s2	0.016 ±0.004	0.023 ± 0.001	n.d.	n.d.	97.5 ± 0.12	0.629 ± 0.02	0.006 ± 0.00	n.d.
BSm38s1 *	69.9 ± 4.83	11.8 ± 0.69	0.034 ±0.001	16.0 ± 4.16	n.d.	0.208 ± 0.004	0.119 ± 0.01	n.d.
BSm38s2 *	85.1 ± 1.40	13.5 ± 0.28	0.037 ± 0.00	n.d.	n.d.	0.214 ± 0.01	0.133 ± 0.01	n.d.
BSm39s1	8.70 ± 1.29	0.277 ± 0.09	n.d.	86.7 ± 1.32	n.d.	0.470 ± 0.10	0.107 ± 0.03	0.231 ± 0.65
BSm39s2	7.65 ± 0.37	0.105 ± 0.001	n.d.	88.9 ± 0.76	n.d.	0.120 ± 0.004	0.029 ± 0.01	0.238 ± 0.67

Table 5 continued: pXRF results for medals 1-60 sides 1 and 2 divided into their types. The wt. % values are the mean of the first and second sets of data, with an error factor 2 standard deviations (2s), as well as the maximum total measurement error for the individual elements based on the reproducibility tests for medals 1-5. n.d. denotes not detected.

Medals	Elements wt. % ± Total Measurement Error							
	Cu ± 1.48	**Zn ± 0.51**	**Ni ± 0.32**	**Ag ± 1.33**	**Al ± 1.47**	**Fe ± 0.11**	**Pb ± 0.05**	**Sn ± 0.04**
MCm40s1 *	63.8 ± 0.68	29.7 ± 0.93	n.d.	5.52 ± 0.14	n.d.	0.030 ± 0.003	0.111 ± 0.03	n.d.
MCm40s2 *	62.2 ± 0.17	30.0 ± 0.08	n.d.	7.02 ± 0.21	n.d.	0.029 ± 0.01	0.112 ± 0.004	n.d.
MCm41s1 *	64.6 ± 0.51	30.8 ± 0.17	n.d.	3.88 ± 0.27	n.d.	n.d.	0.016 ± 0.001	n.d.
MCm41s2 *	64.7 ± 0.22	30.8 ± 0.29	n.d.	3.62 ± 0.23	n.d.	0.025 ± 0.001	0.034 ± 0.02	n.d.
MCm42s1 *w	67.8 ± 0.37	28.8 ± 0.34	n.d.	n.d.	n.d.	0.010 ± 0.03	0.016 ± 0.004	n.d.
MCm42s2 *w	65.3 ± 0.31	30.6 ± 0.15	n.d.	n.d.	n.d.	0.021 ± 0.001	0.023 ± 001	n.d.
MCm43s1 *	47.5 ± 0.12	11.9 ± 0.08	10.1 ± 0.04	28.6 ± 0.39	n.d.	0.163 ± 0.01	0.053 ± 0.01	n.d.
MCm43s2 *	50.3 ± 0.32	13.4 ± 0.16	10.8 ± 0.06	23.8 ± 0.95	n.d.	0.158 ± 002	0.044 ± 0004	n.d.
MCm44s1 *	59.3 ± 2.40	7.87 ± 0.32	n.d.	30.8 ± 2.50	n.d.	0.021 ± 0.06	0.673 ± 0.10	n.d.
MCm44s2 *	64.5 ± 0.17	8.18 ± 0.15	n.d.	25.7 ± 0.30	n.d.	0.031 ± 0.004	0.559 ± 004	n.d.
MCm45s1 w	64.9 ± 0.13	24.1 ± 0.03	8.55 ± 0.00	n.d.	n.d.	0.112 ± 0.02	0.051 ± 0.01	n.d.
MCm45s2 w	65.5 ± 0.06	24.3 ± 0.16	8.60 ± 0.02	n.d.	n.d.	0.093 ± 0.01	0.048 ± 0.01	n.d.
MCm46s1 *	51.8 ± 4.25	6.23 ± 0.24	0.048 ± 0.00	36.0 ± 4.93	n.d.	0.056 ± 0.02	0.220 ± 0.03	n.d.
MCm46s2 *	42.5 ± 0.60	5.51 ± 0.02	0.029 ± 0.08	41.6 ± 0.03	n.d.	0.071 ± 0.03	0.239 ± 0.003	n.d.
MCm47s1 *	77.0 ± 0.17	9.40 ± 0.23	0.081 ± 0.01	12.2 ± 0.38	n.d.	0.171 ± 0.01	0.065 ± 0.01	n.d.
MCSm47s2 *	77.4 ± 0.43	9.36 ± 0.03	0.076 ± 0.01	11.8 ± 0.06	n.d.	0.185 ± 0.01	0.064 ± 0.01	n.d.
MCm48s1	14.7 ± 0.19	0.046 ± 0.00	31.0 ± 0.40	n.d.	n.d.	52.8 ± 1.14	n.d.	0.008 ± 0.02
MCm48s2	15.4 ± 0.39	0.071 ± 0,04	26.1 ± 1.82	n.d.	n.d.	56.4 ± 1.03	n.d.	0.008 ± 0.02
MCm49s1 *	52.0 ± 1.24	18.4 ± 0.56	7.06 ± 0.17	20.4 ± 2.39	n.d.	0.075 ± 0.01	0.174 ± 0.02	n.d.
MCm49s2 *	52.2 ± 1.04	18.3 ± 0.29	6.82 ± 0.15	20.8 ± 1.36	n.d.	0.073 ± 0.01	0.182 ± 0.01	n.d.
MCm50s1 *	79.2 ± 0.43	9.83 ± 0.12	n.d.	10.1 ± 0.15	n.d.	n.d.	0.140 ± 0.01	n.d.
MCm50s2 *	81.0 ± 0.74	9.76 ± 0.06	n.d.	8.40 ± 1.00	n.d.	0.012 ± 0.03	0.114 ± 0.01	

Table 5 continued: pXRF results for medals 1-60 sides 1 and 2 divided into their types. The wt. % values are the mean of the first and second sets of data, with an error factor 2 standard deviations (2s), as well as the maximum total measurement error for the individual elements based on the reproducibility tests for medals 1-5. n.d. denotes not detected.

Medals	Elements wt. % ± Total Measurement Error							
	Cu ± 1.48	**Zn ± 0.51**	**Ni ± 0.32**	**Ag ± 1.33**	**Al ± 1.47**	**Fe ± 0.11**	**Pb ± 0.05**	**Sn ± 0.04**
Dm51s1	98.1 ± 0.69	0.06 ± 0.17	n.d.	n.d.	0.721 ± 2.04	0.540 ± 0.04	0.076 ± 0.001	n.d.
Dm51s2	98.0 ± 1.3	0.04 ± 0.11	n.d.	n.d.	0.714 ± 2.02	0.482 ± 0.06	0.063 ± 0.01	n.d.
Dm52s1 w	86.7 ± 0.56	11.2 ± 0.64	0.062 ± 0.01	n.d.	n.d.	0.098 ± 0.001	0.289 ± 0.05	0.124 ± 0.004
Dm52s2 w	87.0 ± 0.56	11.9 ± 0.08	0.056 ± 0.01	n.d.	n.d.	0.092 ± 0.01	0.368 ± 0.01	0.159 ± 0.01
Dm53s1	0.309 ± 0.01	0.03 ± 0.01	n.d.	n.d.	n.d.	0.166 ± 0.04	1.682 ± 0.14	93.85 ± 0.54
Dm53s2	0.305 ± 0.01	0.04 ± 0.02	n.d.	n.d.	n.d.	0.147 ± 0.07	1.443 ± 0.30	94.45 ± 1.25
Dm54s1 w	67.9 ± 0.27	30.5 ± 0.24	0.054 ± 0.01	n.d.	n.d.	0.123 ± 0.001	0.656 ± 004	0.204 ± 0.003
Dm54s2 w	67.4 ± 0.06	30.8 ± 0.11	0.052 ±0.002	n.d.	n.d.	0.103 ± 0.001	0.674 ± 0.01	0.202 ± 0.004
Dm55s1	98.1 ± 0.01	n.d.	0.085 ± 0.01	n.d.	n.d.	0.019 ± 0.01	0.613 ± 0.01	0.058 ± 0.02
Dm55s2	98.0 ± 0.55	n.d.	0.086 ± 0.01	n.d.	n.d.	0.021 ± 0.02	0.712 ± 0.00	0.062 ± 0.01
Dm56s1	89.8 ± 0.28	6.37 ± 0.01	0.078 ± 0.00	n.d.	n.d.	0.092 ± 0.00	0.518 ± 0.01	1.88 ± 0.01
Dm56s2	89.6 ± 1.43	6.67 ± 0.78	0.083 ± 0.01	n.d.	n.d.	0.111 ± 0.01	0.509 ± 0.02	1.84 ± 0.00
Dm57s1 *	65.1 ± 0.06	12.9 ± 0.10	16.2 ± 0.11	3.61 ± 0.12	n.d.	0.061 ± 0.01	0.018 ± 0.00	n.d.
Dm57s2 *	65.8 ± 0.10	12.9 ± 0.10	16.5 ± 0.03	3.47 ± 0.35	n.d.	0.065 ± 0.01	0.024 ± 0.001	n.d.
Dm58s1 *	59.8 ± 0.48	30.9 ± 0.33	0.013 ± 0.04	7.88 ± 0.75	n.d.	0.031 ± 0.001	0.080 ± 0.001	n.d.
Dm58s2 *	59.4 ± 0.39	30.4 ± 0.07	0.030 ± 0.01	9.18 ± 0.51	n.d.	0.031 ± 0.004	0.070 ± 0.01	n.d.
Dm59s1 *w	65.0 ± 0.52	31.9 ± 0.11	n.d.	1.37 ± 3.87	n.d.	0.071 ± 0.01	0.026 ± 0.01	n.d.
Dm59s2 *w	64.9 ± 0.03	32.4 ± 0.09	0.010 ± 0.03	n.d.	n.d.	0.073 ± 0.01	0.032 ± 0.003	n.d.
Dm60s1 *	80.0 ± 1.14	12.5 ± 0.12	n.d.	5.41 ± 1.71	n.d.	0.030 ± 0.01	0.008 ± 0.02	n.d.
Dm60s2 *	80.7 ± 1.71	12.5 ± 0.11	0.012 ± 0.03	4.70 ± 1.81	n.d.	0.034 ± 0.004	0.017 ± 0.004	n.d.

The semi-quantitative pXRF results combined with the ESEM-EDX mapping and the stereo microscopic examination characterised the 60 religious medals, and distinguished between different types of alloys in the white metal medals. Based on the major and minor elements tabulated above, eight different types of alloys were identified. The results for the 60 religious medals indicate that the predominant types of alloys used are Cu-Zn alloys or brass, followed by Cu-Zn-Ni alloys or 'nickel silver'. There are 32 Cu-Zn alloys or brass medals, of which 24 appear to have silver plating remaining based on the pXRF results combined with the stereo microscopic examination and ESEM-EDX mapping of the medals. Some of the other eight Cu-Zn alloy medals may have had silver plating, but the surfaces are highly worn and further analysis is required. There are 12 Cu-Zn-Ni alloys or nickel silver medals, of which 11 have evidence of silver plating, while one has a worn, inconclusive surface. The next most numerous types are five high Cu alloy medals and five high Al alloy medals. The five Al alloy medals do not appear to have silver plating, but there are traces of a surface deposit remaining in the recesses of the decoration on two of the Al medals. With the five Cu alloy medals, one may have been silver plated, one may have been patinated, and the other three appear to be non-plated. There are three Cu-Ni alloys, two with silver plating and one that appears to be non-plated. The remaining three medals are unusual alloys and do not appear to be silver plated: one high Ag-Cu alloy with > 85 wt. % Ag; one Fe-Ni-Cu alloy with > 50 wt. % Fe and one high Sn-low Pb alloy with > 90 wt. % Sn. The numbers of medals in the different stylistic groups with these types of alloys are shown in **Figure 18**. Patterns in the types of alloys used for the stylistic groups of religious medals need to be examined in further detail, as the study group of 60 medals from a collection of approximately 20 000 was relatively small.

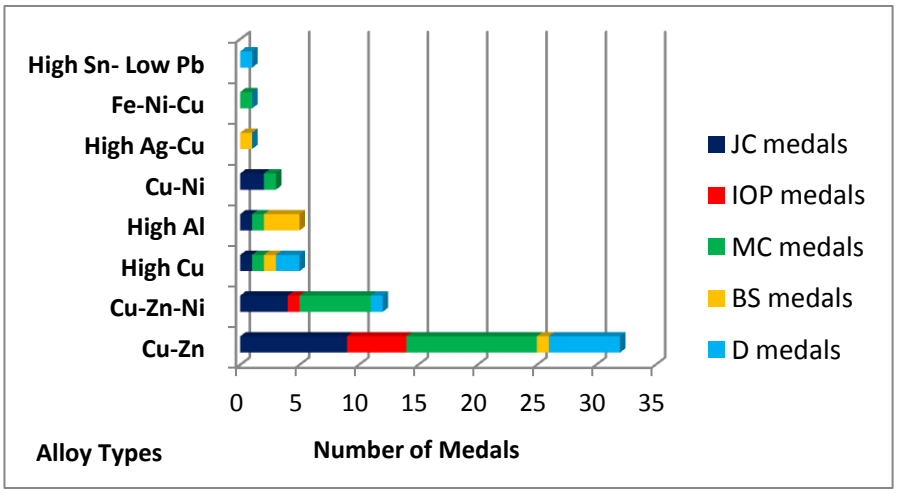


Figure 18: Numbers of medals in the stylistic groups with the different types of alloys indicated by the pXRF results, ESEM-EDX mapping and the stereo microscopic examination. The abbreviations used for the different types of medals are: JC – Jesus Christ medals; IOP – Infant of Prague medals; MC – Madonna and Child medals; BS – Blessed Sacrament medals; D – Diverse medals.

3.6.2 Cluster Analysis of the pXRF Results

Multivariate analysis was carried out on the pXRF results for 28 of the modern religious medals with surfaces that are non-plated or highly worn with the base metal exposed and no silver plating present or only minor traces left in the recesses of the decoration to interfere with the pXRF results for the base metal. Clustan Graphics 8 software provided by the Science Faculty at the University of Lincoln was used, to see if there were patterns or distinct groupings in the base metal alloys of these medals. The cluster analysis was carried out on the first and second sets of data for sides one and two of the 28 medals, with the 8 major and minor elements Cu, Zn, Ni, Ag, Al, Fe, Pb and Sn included as variables. The pXRF results were standardized to z scores, then analysed using squared Euclidean distance and increase in sum of squares (Colston, 2013).

The results of the cluster analysis indicated that the first and second sets of pXRF data are consistent with seven distinct clusters or groups of alloys identified. The dendrogram for the cluster analysis of the 28 medals with the 8 major and minor elements as variables is shown in **Figure 19** and the corresponding scatter plot of the seven clusters is shown in **Figure 20**.

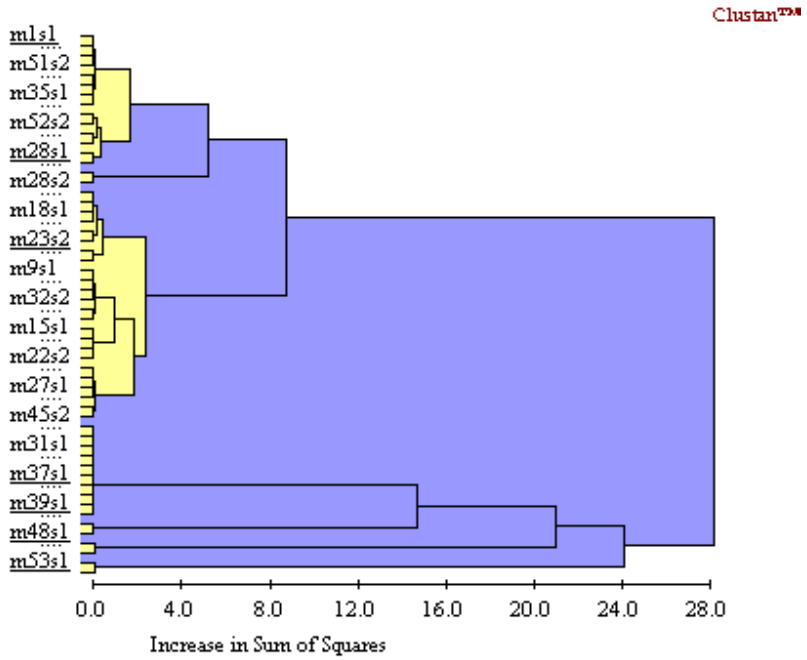


Figure 19: Dendrogram for the cluster analysis of the pXRF results for the first and second sets of data on sides one and two of the 28 medals with non-plated or highly worn surfaces exposing the base metal, using Clustan Graphics 8 software provided by the Science Faculty at the University of Lincoln.

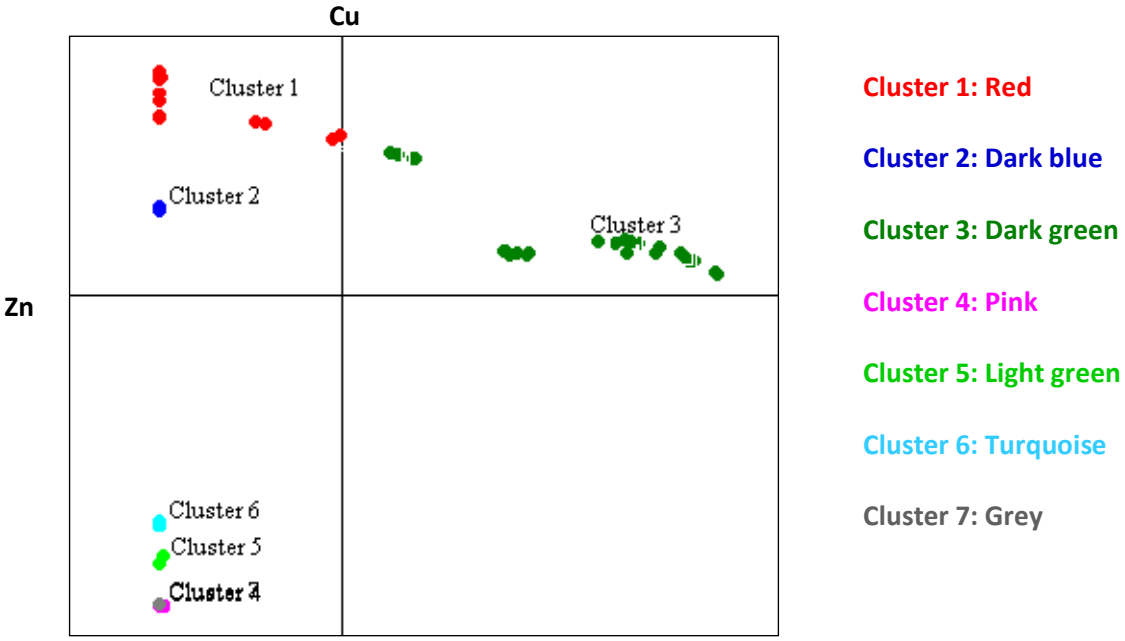


Figure 20: Scatter plot of the seven clusters for the 28 medals with 8 elements Cu, Zn, Ni, Ag, Al, Fe, Pb and Sn as variables. Clusters 4 (high Al alloys) and 7 (High Sn-low Pb alloy) overlap and are outliers along with clusters 5 (high Ag-Cu alloy) and 6 (Fe-Ni-Cu alloy).

The types of alloys represented by the seven clusters and the medals in each cluster are as follows, where m1s1 = medal 1 side 1 and m1s2 = medal 1 side 2 and so on:

Cluster 1: Cu alloys with > 90% Cu and Cu-Zn alloys with > 85 wt. % Cu and <15 wt. % Zn
m1s1 m1s2 m51s1 m51s2 m33s1 m33s2 m35s1 m35s2 m52s1 m52s2 m56s1 m56s2 m55s1 m55s2

Cluster 2: Cu-Ni alloy with > 70 wt. % Cu and > 20 wt. % Ni
m28s1 m28s2

Cluster 3: Cu-Zn with < 85 wt. % Cu, > 15 wt. % Zn and Cu-Zn-Ni alloys with < 85 wt. % Cu, > 15 wt. % Zn and < 15 wt. % Ni
m6s1 m6s2 m18s1 m18s2 m23s1 m23s2 m54s1 m54s2 m9s1 m9s2 m32s1 m32s2 m42s1 m42s2 m15s1 m15s2 m22s1 m22s2 m16s1 m16s2 m27s1 m27s2 m45s1 m45s2

Cluster 4: Al alloys with > 90 wt. % Al
m3s1 m3s2 m31s1 m31s2 m34s1 m34s2 m37s2 m37s1 m36s1 m36s2

Cluster 5: High Ag-Cu alloy with > 85 wt. % Ag and < 15 wt. % Cu
m39s1 m39s2

Cluster 6: Fe-Ni-Cu alloy with > 50 wt. % Fe, > 25 wt. % Ni and < 15 wt. % Cu
m48s1 m48s2

Cluster 7: High Sn-low Pb alloy with > 90 wt. % Sn and 1-2 wt. % Pb
m53s1 m53s2

These seven clusters correlate with the eight different types of plated and non-plated alloys identified by the pXRF results, ESEM-EDX mapping and the stereo microscopic examination, shown in Figure 18, since the high Cu alloys are grouped with the high Cu-Zn alloys in cluster 1.

3.6.3 Elemental Mapping of Plated and Corroded Surfaces using ESEM-EDX

Medals 2, 10, 13, 16, 26, 27, 38, 41, 42, 43, 53 and 54 were analysed by ESEM-EDX mapping and the results assisted in the characterisation of these religious medals by indicating the presence and extent of silver plating on the medals with worn surfaces, as well as the presence of sulphur and chlorine on medals with tarnished and corroded surfaces. This suggests corrosion products such as sulphides and chlorides, which correlates with the appearance of the medals. The results of the ESEM-EDX mapping for medal 16 illustrates the way this technique complemented the pXRF results, as Ag was not detected in the pXRF analysis, but was indicated in the recesses of the decoration on the surface of the medal by the ESEM-EDX mapping. It was difficult to determine if there was silver plating present on medals such as this in the stereo microscopic examination, as the base metal is a Cu-Zn-Ni alloy or 'nickel silver' which is a silvery white colour and not easy to visually distinguish from silver plating or high silver alloys. An ESEM-EDX photomicrograph of the proper right (P.R.) side of Christ's head on side 1 of medal 16 is shown in **Figure 21a**, next to the ESEM-EDX mapping for Ag in the same area in **Figure 21b.**

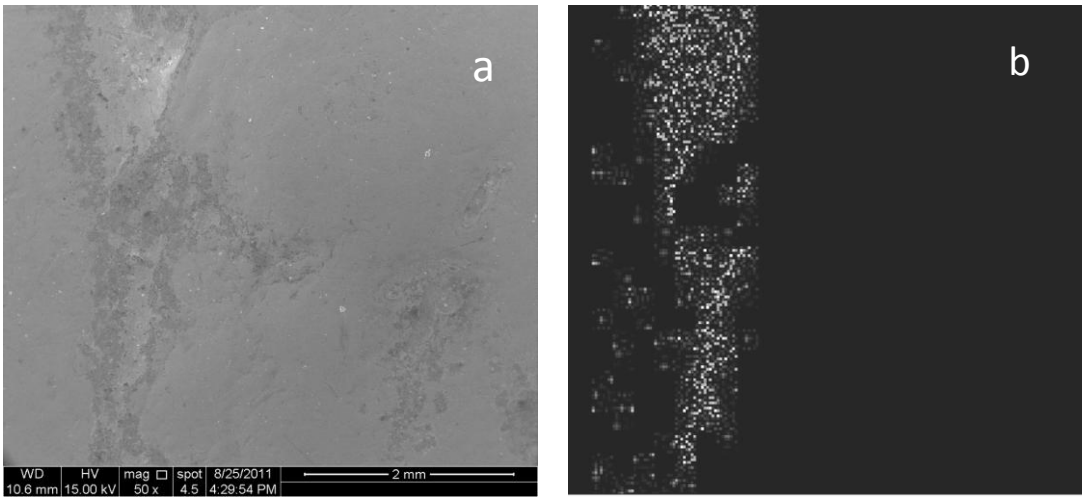
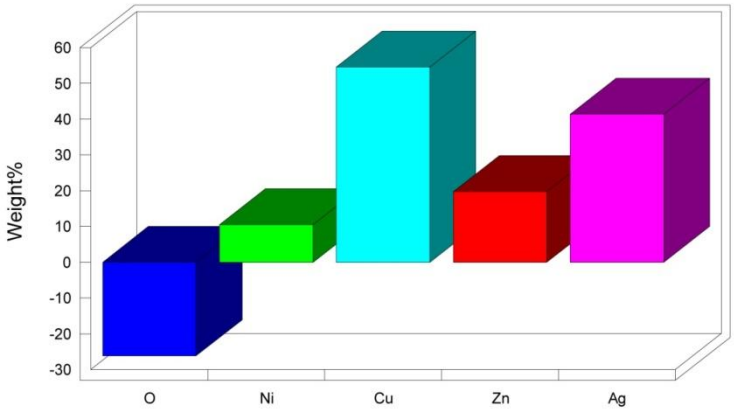


Figure 21a: ESEM-EDX photomicrograph of medal 16 side 1 - P.R. side of Christ's head at 50x;
Figure 21b: ESEM-EDX silver mapping of the same area on medal 16 side 1 showing the traces of silver plating in the recesses of the decoration.

A graph of the ESEM-EDX results for the elements identified in this area, including silver (Ag) is shown in **Figure 22** and a digital photograph of medal 16 side 1 overall is shown in **Figure 23.**



Element	Weight%
O K	-26.19
Ni K	10.48
Cu K	54.60
Zn K	19.70
Ag L	41.41
Totals	100.00

Figure 22: The semi-quantitative results for the ESEM-EDX mapping of proper right side of Christ's head on side 1 of medal 16 at 50x, indicating the presence of silver (Ag) plating and copper (Cu), zinc (Zn) and nickel (Ni) in the same ratios identified in the pXRF analysis.

Figure 23: Medal 16 side 1 overall: 65.5 wt. % copper ± 1.48 %; 22.6 wt. % zinc ± 0.51 %; 10.7 wt. % nickel ± 0.32 %. The wt. % for these elements are based on the mean values of the first and second sets of pXRF data, with the total measurement error factors based on the pXRF results of the reproducibility tests for medals 1-5.

The ESEM-EDX mapping indicated the presence of silver corrosion products on medals such as medals 43, which was identified as a silver plated Cu-Zn-Ni alloy or nickel silver by the pXRF results. An ESEM-EDX photomicrograph of an area analysed on side 1 of medal 43 is shown in **Figure 24a,** next to the ESEM-EDX mapping for Ag in the same area in **Figure 24b.** The ESEM-EDX mapping of medal 43 side 1 indicated a loss of silver plating on the high points of the surface, as well as the presence of sulphur on this medal. This is consistent with the dark grey-black tarnished surface of Medal 43, suggesting the corrosion products could be silver sulphide.

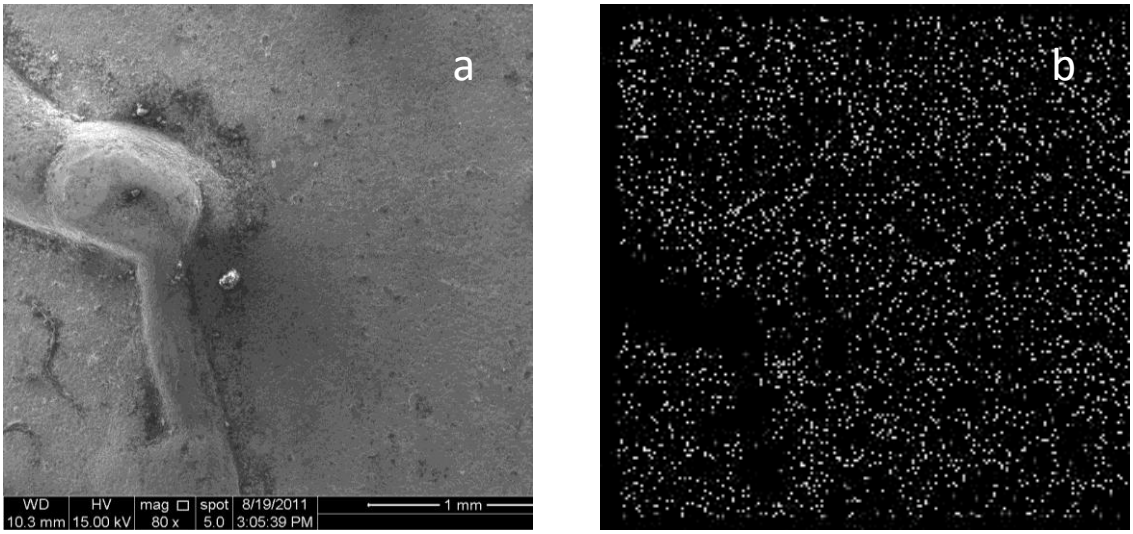
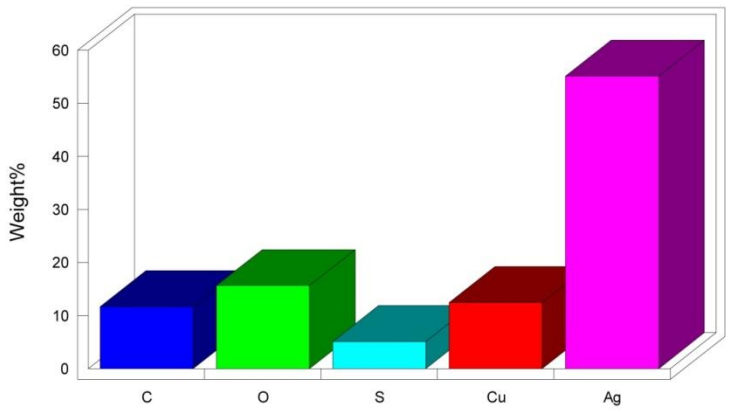


Figure 24a: ESEM-EDX photomicrograph of medal 43 side 1 - proper left (P.L.) hand of the Jesus at 80x

Figure 24b: ESEM-EDX silver (Ag) mapping of the same area on medal 43 side 1 showing the P.L. hand of Jesus at 80x outlined by the silver plated remaining.

A graph of the ESEM-EDX results for the elements identified in this area on medal 43, including silver (Ag) and sulphur (S) is shown in **Figure 25** and a digital photograph of medal 43 side 1 overall is shown in **Figure 26.** Only the alloy type is given for this medal due to the presence of silver plating and corrosion products on the surface.



Element	Weight%
C K	12.58
O K	17.56
S K	5.39
Cu L	10.14
Ag L	54.34
Totals	100.00

Figure 25: The semi-quantitative results for the ESEM-EDX mapping of the proper left hand of Jesus on medal 43 side 1 at 80x, indicating the presence of silver (Ag) and sulphur (S).

Figure 26: Medal 43 side 1: silver plated copper-zinc-nickel or nickel silver alloy with dark grey-black corrosion products.

Other types of corrosion products were indicated by the ESEM-EDX analysis of the medals, such as chloride corrosion on medal 26, which correlates with the presence of raised green surface deposits on both sides of this medal. Medal 26 was identified as a Cu-Zn alloy with silver plating by the pXRF analysis, but the results did not indicate elements such as sulphur (S) or chlorine (Cl), which could account for the tarnish and corrosion products. An ESEM-EDX photomicrograph of an area of the green surface deposit analysed on side 1 of medal 26 is shown in **Figure 27a,** next to the ESEM-EDX mapping for chlorine (Cl) in the same area in **Figure 27b.** A graph of the ESEM-EDX results for the elements identified in this area of medal 26, including chlorine (Cl) and sulphur (S) is shown in **Figure 28** and a digital photograph of medal 26 side 1 overall is shown in **Figure 29.** Only the alloy type is given for this medal due to the presence of silver plating and corrosion products on the surface. The ESEM-EDX mapping of medal 26 side 1 indicated the presence of chlorine (Cl) and sulphur (S) on this medal, which is consistent with the dark grey-black tarnished surface and the green corrosion, suggesting the corrosion products could include dark grey-black silver sulphides and green copper chlorides.

The ESEM-EDX mapping also indicated silver plating on medals 13, 27 and 42; sulphur corrosion on medals 2 and 10; chloride and sulphide corrosion on medals 38 and 54, as well as the presence of elements such as potassium (K) on medal 41 and calcium (Ca) on medals 26 and 53. The ESEM-EDX mapping results for the medals are included in section 6.1.6 of the Appendices.

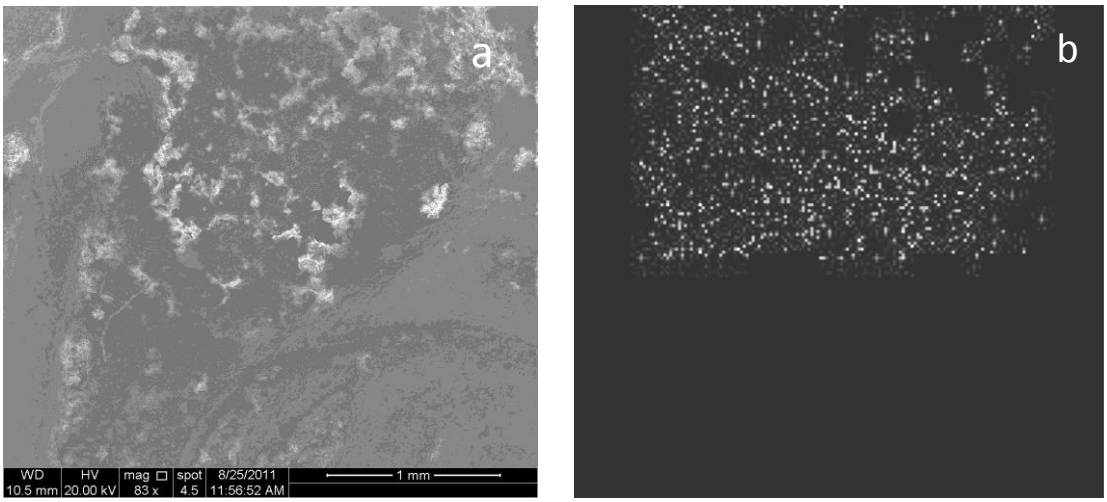
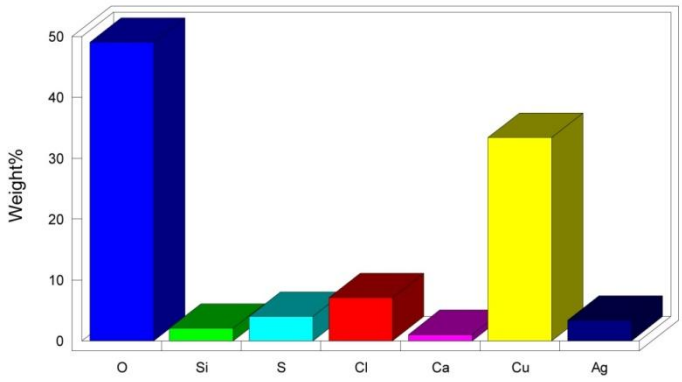


Figure 27a: ESEM-EDX photomicrograph of medal 26 side 1 – area of green corrosion adjacent to the proper right side of the Virgin Mary's head at 83x
Figure 27b: ESEM-EDX chlorine (Cl) mapping of part of the same area on medal 26 side 1.



Element	Weight%
O K	49.06
Si K	2.07
S K	3.99
Cl K	7.05
Ca K	1.01
Cu K	33.44
Ag L	3.38

Figure 28: The semi-quantitative results for the ESEM-EDX mapping of the area of green corrosion adjacent to the proper right side of the Virgin Mary's head on medal 26 side 1 at 83x, indicating the presence of chlorine (Cl), sulphur (S), copper (Cu) and silver (Ag), as well as calcium (Ca) and silicon (Si).

Figure 29: Medal 26 side 1: silver plated Cu-Zn alloy such as brass with spots of green copper corrosion adjacent to the proper right side of the Madonna's head.

3.7 Conclusions

The pXRF analysis provided reproducible semi-quantitative and qualitative results characterising the alloys used in the 60 modern religious medals and identified the following different types of alloys for the white metal medals: silver plated copper alloys such as brass; silver plated and non-plated copper-zinc-nickel alloys such as nickel silver; silver plated and non-plated copper-nickel alloys; non-plated aluminium alloys; non-plated, silver plated and patinated copper alloys; one non-plated high silver-low copper alloy; one non-plated iron-nickel-copper alloy and one non-plated high tin-low lead alloy. Examples of white metal medals in the study group with these types of alloys are shown in **Figure 30**, illustrating the diversity and the way that the same stylistic type of medal can be made of different alloys. For example the upper Cu-Zn alloy medal and the lower Cu-Ni alloy medal.

Combined with the ESEM-EDX mapping of 12 medals and the stereo microscopic examination of all 60 medals, the pXRF results indicate that the predominant types of alloys are copper-zinc alloys such as brass, with 32 medals identified. This is followed by 12 copper-zinc-nickel alloys or nickel silver medals. These two types of alloys account for the 44 of the 60 medals. The next types of alloys identified in terms of numbers were five almost pure copper alloys and five almost pure aluminium alloys. These two alloy types appear to have been used for many of the larger religious medals, such as the Blessed Sacrament medals. The remaining medals were identified as three copper-nickel alloys; one high silver-copper alloy; one high iron-nickel-copper alloy and one high tin-low lead alloy. With only two medals identified with > 1 wt. % tin, the pXRF results suggest the limited use of this metal in the production of the modern religious medals.

Figure 30: Examples of the different types of alloys identified by the pXRF analysis for white metal medals in the study group of 60. Slide taken from the paper presented at the ICOM Metal 2013 Conference in September 2013 entitled 'The Non-Invasive Characterisation of a Collection of 20th Century Religious Medals for an Online Museum Catalogue using X-ray Fluorescence Spectroscopy'.

Although the study group was limited to 60 religious medals from a collection of approximately 20 000, the range of alloys used to produce the 60 medals appears to reflect some of the developments in metalworking technology in the 20th century. For example, the increased production of aluminium alloys during the First and Second World Wars, which lead to the use of aluminium in the 20th century in the manufacture of a wide range of decorative and utilitarian metal objects as it became more economically viable (Duncan, 1988:27; Selwyn, 2004: 43). Some of the earliest aluminium alloys contained iron (Duncan, 1998:27), as do two of the aluminium medals in the study group, Jesus Christ medal 3 and Madonna and Child medal 31. These two medals may therefore date to the early part of the 20th century when this type of aluminium alloy was produced. The possibility of metal recycling however complicates dating the religious medals based on alloy types alone.

The development and increased use of other economical alloys in the 20th century is also reflected in the different alloys used in the white metal medals. For example, alloys made of

combinations of copper, zinc and nickel such as nickel silver and copper-nickel alloys. Both these types of alloys replaced more expensive alloys containing silver for a range of small metal objects including jewellery and coinage during the 20th century. In the mass production of modern coinage, which is comparable with the production of the religious medals, the high percentages of silver used in the 19th century were greatly reduced or eliminated in the 20th century in a number of countries, such as Britain (Selwyn, 2004: 133; Janeiro Coins & Bullion, 2014). British silver coins pre 1920 contained 92.5 % silver, that is, Sterling silver, while from 1920 to 1946 they contained 50 % silver and from 1947 to 1971 they contained no silver as copper-nickel alloys were used. After the decimalisation of British coinage in 1971 copper-nickel alloys continued to be used and there was no silver present in the coins (Janeiro Coins & Bullion, 2014).

The production and increased use of alloys which have good corrosion resistance was another development in the metalworking industry in the 20th century, such as alloys containing nickel in combination with metals such as copper, zinc, iron, chromium and molybdenum (Selwyn, 2004: 127-128). The production of alloys made of nickel combined with copper and zinc, as well as iron are relevant as there are 16 religious medals containing nickel in combination with these metals, including one medal made of an unusual iron-nickel-copper alloy, which is one of the white metal medals shown in Figure 30. Copper-nickel alloys were used in the production of modern coinage by the mid 20th century as outlined above, and copper-zinc-nickel alloys such as nickel silver were in use from the early 1900's for ornamental metal objects and for decorative architectural elements until the mid 1950's. Both these types of alloys are silvery white, but can be electroplated with silver (Selwyn, 2004: 57-58). This is evident in the religious medals in the study group as 11 of the 12 medals made of nickel silver have silver plating or traces of silver plating remaining, as well as two of the three medals made of copper-nickel alloys. The white metal medals shown in Figure 30 illustrate this, as the three copper-zinc-nickel or nickel silver medals and the upper and lower copper-nickel medals have evidence of silver plating.

The relatively limited use of metals such as tin in the alloys used for the religious medals suggested by the pXRF results may also be due to developments in the metal industry in the 20th century. The availability of tin for items such as religious medals in Britain and Europe may have been affected by the decline in the tin mining industry in Britain in the 1930's (Mining Artifacts and History, 2014). The 1897 date of the one medal made of a high tin-low lead alloy, Diverse medal 53, which commemorates Queen Victoria's diamond jubilee on one side and depicts the Guisborough Abbey on the other, is consistent with this as the production

of tin was booming during the second half of the 19th century (Mining Artifacts and History, 2014). After the decline in the tin industry in the 1930's the comparative availability of other metals such as copper, zinc, nickel, aluminium, iron, lead and silver, which were identified in the alloys for the majority of the religious medals, may have lead to a predominance of alloys made of these metals for the mass production of inexpensive metal items such as the religious medals. The relatively small size of the study group of 60 medals from the collection of approximately 20 000 may also be a factor in the limited identification of tin in the pXRF results and analysis of additional medals is recommended before definitive conclusions can be drawn concerning the use of tin in the production of the modern religious medals.

With regard to the provenance and date of the modern religious medals, it is difficult to draw specific conclusions due to the lack of reference data published in English on the different stylistic types and their origin, as well as the limited size of the study group. With the exception of two commemorative medals dated to the second half of the 19th century, that is, Diverse medal 51 made of an almost pure copper alloy dated to 1862 and Diverse medal 53 made of a high tin-low lead alloy dated to 1897, the study group of religious medals are dated to the 20th century up until the 1970's. The elongated oval shaped medals such as Infant of Prague medals 19 and 20 and Madonna and Child medal 42 may be dated to around the middle of the 20th century as suggested by similarities with the religious medal shown in the photograph in Figure 1 taken by Paul Strand in the Outer Hebrides in Britain in 1954. A mid 20th century date for some of the medals is supported by the inclusion of the date 1950 on side 2 of Diverse medal 59. While medals made of copper alloys with minor amounts of phosphorous and tungsten such as Blessed Sacrament medal 35 and Madonna and Child medal 33 may date closer to the 1970's, as this is a relatively recent alloy type (Bailey, 2013). The comparatively good condition and bright golden surface of Blessed Sacrament medal 35 are consistent with a later date.

The majority of the religious medals in the study group appear to be European, originating or intended for use in countries such as Britain, France, Italy and Germany. In addition, Infant of Prague medal 22 is an example of a medal from the U.S. as there is an inscription 'NEW HAVEN CONN.' on side 2. The visual and stereo microscopic examination of the 60 medals indicated that there are 29 medals with inscriptions or texts in languages other than Latin. Of these 29 medals there are 13 medals with inscriptions or text in English. The majority of these medals appear to have been struck and they are made of a range of alloy types, including five silver plated and non-plated copper-zinc alloys such as brass; 4 non-plated aluminium alloys; two non-plated copper alloys; one silver plated copper-zinc-nickel alloy or nickel silver and one non-plated high tin-low lead alloy. This is followed by eight medals including text in French or

the word ‘FRANCE’ as well as one medal with the word ‘LYON’. These medals also appear to have been struck. Six of them are made of silver plated copper-zinc alloys such as brass; two are made of silver plated copper-zinc-nickel alloys such as nickel silver and one is a non-plated aluminium alloy. There are four medals with the word ‘ITALY’ and one medal with the text in Italian including the word ‘Roma’ and the date 1950, as mentioned above. All five of these medals are made of silver plated copper-zinc alloys such as brass and the planchets may have been cast prior to striking the design of the medal. There is one medal with the text in German, which is made of a non-plated copper-zinc alloy such as brass and it appears to have been struck. The American medal is also made of a copper-zinc alloy such as brass that was struck and may have once been silver plated. Attributing the provenance of the religious medals based on these inscriptions and texts is not always straight forward, as the Infant of Prague medals 19 and 20 have the text ‘Infant of Prague’ in English as well as the word ‘ITALY’ in English. This suggests that they may have been made in Italy for use in an English speaking country such as Britain, as religious medals were ordered from different production centres in Europe for use in other countries (Ajmar and Sheffield, 1994: 40). Another example is Jesus Christ medal 15 which has the Lord’s Prayer in English on side 2, as well as the word ‘FOREIGN’, which may be an indication that it was an import (Attwood, 2014). A more detailed examination of the provenance and date of the religious medals will be possible when curatorial staff at the University Museum of Bergen catalogue the entire collection of modern religious medals (von Achen, 2011).

Conclusions about the manufacturing techniques used for some of the modern religious medals are limited by the worn and abraded surfaces of the medals, while the relationship between the manufacturing techniques and the alloy types and stylistic types is limited by the relatively small study group of 60 out of 20 000 medals. However given these limitations it appears that the modern religious medals in the study group were all struck between two die, with the possible exception of Diverse medal 56 which may have been cast. The appearance of this medal is quite distinct from the rest of the study group, as it has a considerable amount of a dark brown resinous material in the recesses of the surface decoration. The style of the medal is also unusual and it could be an example of a cast medal which was not mass produced and was made at a later date. The blanks or planchets used for some of the medals may also have been cast before striking, rather than cut or stamped from sheet metal. For example a number of the 32 medals made of copper-zinc alloys such as brass, as well as some of the 12 copper -zinc-nickel alloys or nickel silver medals and the three copper-nickel alloys. All five of the aluminium alloy medals and the five copper alloy medals appear to be struck with the majority of both alloy types having a rimmed edge similar to coins. The three unusual

alloy types in the study group, that is, the high silver-low copper medal, the iron-nickel-copper medal and the high tin-low lead medal also appear to have been struck. In addition, Blessed Sacrament medal 39 which is made of a high silver-low copper alloy has incised details in the floral decoration on side 1. Jesus Christ medal 17 also appears to be made of a combination of techniques, as the relatively high relief figure of Christ appears to have been cast and riveted onto the background of the medal which was struck.

Several of the religious medals also have defects or imperfections which indicate that they were struck, such as borders or decorative edges that are slightly off centre, for example on side 2 of Jesus Christ medal 9, which is made of a copper-zinc alloy such as brass that may have once been silver plated or on side 2 of Jesus Christ medal 11, which is also a copper-zinc alloy such as brass that was silver plated. Fine jagged, raised lines on the surface can also indicate that a medal was struck as these can be caused by cracks in the die (Headley, 2014). For example on the lower part of side 2 on Jesus Christ medal 6, which is made of a copper-zinc alloy such as brass with traces of silver plating and on side 2 of Jesus Christ medal 15, which is also made of a copper-zinc alloy or brass that may have once been silver plated.

The pXRF analyses combined with the ESEM-EDX mapping and stereo microscopic examination indicated that 38 medals have evidence of silver plating remaining, that is more than half of the study group of 60. The most likely technique used for silver plating the modern religious medals is electroplating, which was developed in the 19th century and patented in 1840 by Elkington and Co. in Birmingham, England (Lewis, 1988: 39; Selwyn, 2004: 135). It became a widely used method of silver plating in the 20th century as it was economical and could produce a thin, even layer of silver on different types of base metal alloys such as those identified by the pXRF analysis for the modern religious medals. The absence of mercury in the pXRF results for the silver plated copper alloy medals suggests that pre-treatment with mercury salts (Selwyn, 2004: 135) was not part of the silver electroplating process for the religious medals made of this type of alloy. The presence of silver plating on the majority of the religious medals, combined with the use of silvery white coloured alloys may suggest an adherence to tradition in the appearance of the modern religious medals, as the earliest medals thought to be of a religious or devotional nature dated to the Renaissance period were made of silver as well as bronze (New World Encyclopedia, 2013). When religious medals began to be mass produced in the 19th century silver alloys were still used for religious medals, as well as the more predominant copper alloys (Ajmar and Sheffield, 1994:41). However it may also be due to more practical reasons such as the relative low cost of silver plated base metal jewellery and ornamental items in the 20th century.

The worn, tarnished or corroded condition of the medals has resulted in the loss of the silver plating, as well as a lack of homogeneity on the surface of some of the medals. This needs to be considered when drawing conclusions from the pXRF analysis, in particular regarding the silver plating, as there are traces of silver in the recesses of the decoration on some medals, but silver was not identified in the pXRF analysis. This could be due to the positioning of the medals so that central areas with exposed base metal were analysed rather than the recesses of the decoration where traces of silver plating remain. The ESEM-EDX mapping therefore provided valuable complementary information on the medals analysed by pXRF, confirming the presence of traces of silver plating on several medals with highly worn surfaces, as well as indicating that the tarnish and corrosion products included sulphides and chlorides, which is consistent with the appearance of the medals.

The pXRF results for the 60 modern religious medals therefore need to be interpreted in combination with the ESEM-EDX mapping and the stereo microscopic examination, due to the limitations involved in the pXRF analysis of plated, patinated, heat-treated, tarnished or corroded and worn metals. Combining the analytical techniques has provided practical, end user information, which contributes to the collections management of the approximately 20 000 modern religious medals at the University Museum of Bergen and facilitates their inclusion in the online catalogue of the coins and medals. The information gained also assists in the preservation of the religious medals by identifying the types of metal alloys they are made of, as well as indicating the presence of silver plating and corrosion products such as chlorides which can be unstable. This contributes to the decision making process for the conservation of the medals by helping to determine the most appropriate preventive measures and remedial treatments to implement for the different types of alloys, in preparation for the comprehensive social history project planned for the modern religious medals at the University Museum of Bergen.

3.8 Future Research

Further analysis of examples of the different stylistic types of modern religious medals in the collection of the University Museum of Bergen could be carried out to see if there are patterns in the use of certain alloys for specific types, as suggested by the identification of almost pure aluminium and copper for some of the larger types of religious medals such as the Blessed Sacrament medals. Correlations between the types of alloys used for the different stylistic types and the manufacturing techniques, as well as the provenance could be examined in

more detail once a greater number of medals have been examined, catalogued and analysed. With a collection of approximately 20 000, this analysis could start with medals that are non-plated or have surfaces that are highly worn with exposed base metal, to build up a comprehensive reference database on the types of metal alloys used to produce the modern religious medals.

The combined use of complementary analytical techniques such as pXRF, ESEM-EDX mapping and stereo microscopy is recommended, as is a rigorous experimental procedure for the pXRF analysis. This has been recommended in other recent publications on the XRF and pXRF analysis of cultural heritage objects, (Craig et al., 2007: 2020; Goodale et al., 2012: 880; Heginbotham et al., 2011) and includes the use of metal reference standards, regular internal calibration of the analyser, reproducibility tests, the inclusion of error factors, and detailed documentation of the operating parameters. The use of pXRF analysers with silicon drift detectors (SDD) or silicon-PiN diode detectors (PIN), and quantification methodology based on fundamental parameters software calibrated with reference standards is also recommended, as these have been found to produce accurate results (Heginbotham et al., 2011).

Additional ESEM-EDX mapping could be carried out on more of the modern religious medals with worn or inconclusive surfaces to identify the presence of traces of silver plating, as well as indicate the types of corrosion products on tarnished and corroded medals. Further analysis of the corrosion products on the medals could be investigated with analytical techniques such as Raman Spectroscopy (RS) (Stuart, 2007: 154). Analysis of organic deposits on the medals could also be investigated, as several of the medals appeared to have traces of dark brown resinous material on the surface. Preliminary analyses were carried out on several of the medals with resinous surface deposits, for example Jesus Christ medal 14, shown in Figure 2, using non-invasive Fourier transform infrared (FTIR) micro-spectroscopy in the Science Faculty at the University of Lincoln. The results indicated that this technique could be useful to characterise organic deposits on the modern religious medals. Raman spectroscopy may also be useful, as it has been successfully applied to the analysis of both natural and synthetic resins (Stuart, 2007: 148-157). Prior to these analytical techniques being used, a stereo microscopic examination of the religious medals is recommended to gain a visual understanding of the surface before analysis and define the questions being addressed by the analyses, as this proved to be an essential part of the non-invasive characterisation of the modern religious medals.

4.0 Analysing the Effects of Cleaning Treatments in Metals Conservation with Scanning Electron Microscopy Coupled with Energy Dispersive X-ray Spectroscopy

4.1 Introduction

The literature review indicated that there are a limited number of published references on the effects of standard conservation treatments such as the surface cleaning of historic metal objects, with the exception of silver (North, 1980; Wharton et al., 1990; Selwyn and Costain, 1991; Bishop Museum, 1996; Selwyn, 1997, 1999 and 2004). The references on silver are still relevant, in particular the information they provide on the negative side effects of using proprietary products with aggressive abrasives and highly acidic or alkaline chemical components, such as acidified thiourea silver dip solutions and products containing ammonia. However it appears that the results of this research and the subsequent recommendations regarding the cleaning of historic metal surfaces may not be well known or not strictly adhered to in the conservation of historic metal objects. The reasons for this may be a lack of access to international references; the relative speed with which some proprietary products work, such as silver dip; the large size of many historic metal objects or collections of objects that require treatment and the implications these factors can have on the resources available for conservation projects in terms of staff, materials and equipment available for use and budgetary constraints.

An additional factor may be that reading about the effects of cleaning treatments on metal objects in published articles or reports does not always have the same impact as seeing the visual effects on the metal surfaces. Assessing the effects of conservation treatments using visual techniques such as standard laboratory microscopes is a fundamental part of conservation work, but it is perhaps under-used in practice for checking the effects of materials and treatments before their use. In addition the relatively low magnifications of many standard laboratory microscopes may not be sufficient to see the effects of treatments in detail. The examination of the surface of cultural heritage objects being conserved at higher magnifications using analytical techniques such as SEM-EDX is even less common, due to the lack of access to this relatively expensive equipment. The Research MSc therefore provided a valuable opportunity to examine the effects of various surface cleaning treatments used in metals conservation with the ESEM-EDX in the Science Faculty at the University of Lincoln. Adopting this approach was based on previous research carried out for my conservation thesis at the University of Canberra, where the surfaces of iron electrodes before and after treatment

were analysed using SEM-EDX and the results compared with quantitative electrochemical analysis of the corrosion rates during treatment of the iron electrodes using Tafel plot extrapolation and computerized linear least-square techniques. The SEM-EDX results correlated with the electrochemical analysis of the corrosion rates during treatment, in that the surface of the clean iron electrodes treated with the solutions that produced the highest corrosion rates during treatment were the most visibly etched and corroded in the SEM-EDX images at magnifications of 100x, 500x and 1000x (Willey, 1991).

Given this correlation between the SEM-EDX images and the quantitative results of the electrochemical analysis of clean metal surfaces, ESEM-EDX was used to examine the effects of six proprietary products and four conservation preparations on the surface of four different types of metals found in cultural heritage objects. The metals included in the experimental work were silver (Ag), copper (Cu), lead (Pb) and iron (Fe), as these metals are commonly found in historic objects. The proprietary products included in the experimental work were Goddard's Silver Dip; Silvo Silver Polish; Liberon Brass and Copper Polish; Nevr Dull Wadding Polish; Pre-Lim Surface Cleaner and Renaissance Metal De-Corroder. The preparations made up in the conservation laboratory were precipitated calcium carbonate in a paste with ethanol; 5% w/v disodium EDTA in deionised water; 5% w/v disodium EDTA in boiled deionised water and 5% w/v disodium EDTA in boiled deionised water made into a gel with 5 % w/v gel of methyl cellulose (North, 1987: 244; Pearson, 1988). The metal coupons were analysed before and after treatment with these materials using the ESEM-EDX, as well as at two, four and six months after treatment. A control coupon for each type of metal was also analysed using pXRF to document the elemental composition of the test metals.

4.2 Objectives

The objectives were to analyse and visually document the effects of a range of proprietary products and conservation preparations on the surface of different metals found in cultural heritage objects using ESEM-EDX. The idea was to compile a visual database or atlas of the effects of these cleaning treatments at a range of magnifications before and after treatment, as well as over a six month period after treatment to assess any residual effects of the treatments for future reference in metals conservation. Specific questions addressed were to see if the reported negative effects of certain proprietary products and conservation preparations were evident in the ESEM-EDX results, as well as to compare the effects of the proprietary products with the conservation preparations. The ESEM-EDX analyses were designed to provide information that could be incorporated in the decision making process for implementing appropriate conservation treatments for objects with components made of

these types of metals, in particular historic metal objects. The results of the ESEM-EDX analyses were also intended to be presented to students in the Conservation Training Programme at the University of Lincoln, to visually demonstrate the importance of examining the effects of irreversible conservation treatments such as cleaning before their use on cultural heritage objects. In particular, the importance of assessing the pH of solutions used in chemical treatments and the hardness of abrasive components in mechanical treatments compared with the hardness of the metal being treated.

4.3 Materials

4.3.1 Metal Coupons – Silver, Copper, Lead and Iron

Four samples of silver, copper, lead and iron were included in the experimental work. The silver, copper and lead samples were c. 1.0 cm^2 coupons from one piece of sheet metal, similar to the metal coupons used in Oddy testing (Bamberg et al., 1999; Robinet and Thickett, 2003). The iron coupons were slightly larger and thicker, measuring c. 1.5 x 2.5 x 0.28 cm and were prepared from one piece of iron. The coupons of each type of metal were engraved with I, II, III and IV in the upper right corner, for identification during the analyses. The front and back surfaces of each coupon were first degreased with acetone applied on cotton swabs and then the metal coupons were photographed using a digital Olympus E620 camera and a copy stand. The digital photographs of the metal coupons are shown in **Figures 31-34.** Coupons I, II and III were treated with the different cleaning products and coupon IV was left untreated as the control for each type of metal.

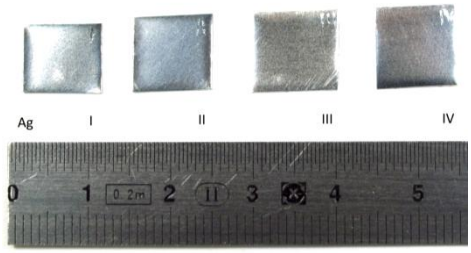


Figure 31: Silver (Ag) coupons before treatment (B.T.)

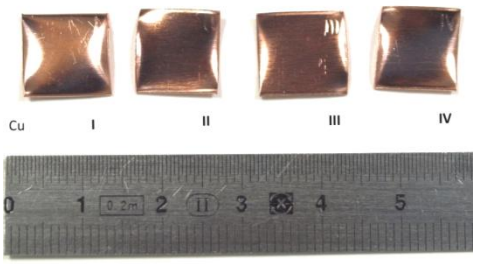


Figure 32: Copper (Cu) coupons before treatment (B.T.)

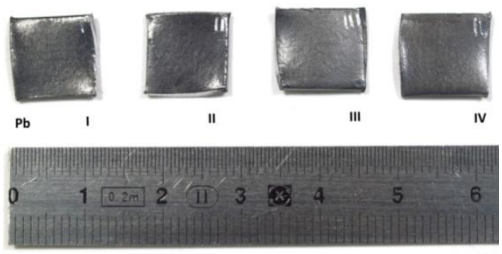


Figure 33: Lead (Pb) coupons before treatment (B.T.)

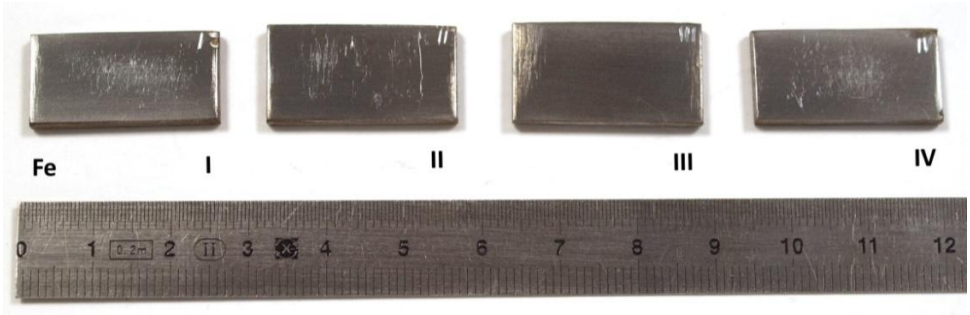


Figure 34: Iron (Fe) coupons before treatment (B.T.)

Bare metal coupons were used rather than tarnished or corroded metal coupons to provide reproducible results that could be directly compared to assess the effects of the different cleaning treatments on each type of metal without the interference of variables due to the tarnish or corrosion, such as variations in the surface area and reactions with the corrosion products. In addition the surface of metal objects requiring conservation treatment is not always completely covered in tarnish or corrosion, in particular historic metal objects which are the focus of this research component rather than archaeological metal objects which can be heavily corroded. For example, historic European silver objects with unevenly tarnished surfaces due to exposure to volatile organic compounds (VOCs) or residues from past cleaning treatments. Medieval lead objects can also have slightly oxidised surfaces in combination with patchy spots of corrosion due to exposure to VOCs. The same applies to some anthropological metal objects that require conservation treatment, for example West African objects made of silver-copper alloys that have slightly tarnished areas in combination with areas of corrosion, or have been cleaned in the past and given an uneven coating of lacquer, which has led to preferential corrosion of the uncoated areas. Navajo silver jewellery can also have varying degrees of tarnish or corrosion, and be regularly cleaned at the request of the Navajo people as a sign of respect for the objects. Archaeological metal objects that have been treated in the past and the corrosion products completely removed can also have bare metal surfaces that need to be protected from inappropriate cleaning if re-treatment is required. For example objects such as solid silver Viking ingots or bars that have been previously cleaned back to bare metal and given an uneven coat of lacquer, which has led to preferential

corrosion of the areas not covered by the lacquer or where the lacquer has deteriorated. All of these types of objects can be difficult to treat as the surface can be patchy and uneven with areas of considerable tarnish or corrosion adjacent to areas of relatively clean metal.

4.3.2 Proprietary Products and Conservation Materials Prepared in the Laboratory

The proprietary products and conservation preparations included in the ESEM-EDX analysis of the effects of metal treatments are listed in **Table 6.** The main components and pH of the materials are taken from the materials safety data sheets and product information. The references for this information are provided in section 6.2 on the Materials and Suppliers for the Research MSc.

Table 6: The proprietary products and conservation preparations included in the ESEM-EDX analysis of the effects of cleaning treatments in metals conservation.

Proprietary Products and Conservation Preparations	**Description**	**Components**	**pH**
Goddard's Silver Dip	Clear solution	Thiourea Sulphuric acid Propanol Non-ionic surfactants	< 2
Silvo Silver Polish Reckitt Benckiser	White suspension	Isopropanol Ammonium Hydroxide Silica quartz Fumed silica	10 - 10.6
Precipitated Calcium Carbonate in Ethanol	White paste	Ethanol Calcium carbonate	-
Liberon Brass and Copper Polish	Buff coloured suspension	Ethanol Phosphoric acid Silica quartz	2.4
Nevr Dull Wadding Polish The George Basch Co, Inc.	Buff coloured cotton fibres with dark inclusions	Petroleum spirits Lubricating oil -oleic acid, palmitic (hexadecanoic) acid Kaolin/China clay Finely ground silica quartz Hematite	-
Pre-Lim Surface Cleaner Picreator Ltd	Light brown paste	Water/White spirits emulsion Neuburg silica chalk	-
5% w/v EDTA in tap water	Clear aqueous solution	Disodium salt of ethyl diamine tetra-acetic acid (EDTA)	4.5
5% w/v EDTA in boiled deionised water	Clear aqueous solution	Disodium salt of ethyl diamine tetra-acetic acid (EDTA)	4.5
5% w/v EDTA in boiled deionised water in a gel with 5% w/v methyl cellulose	Clear aqueous gel	Disodium salt of ethyl diamine tetra-acetic acid (EDTA) Methyl cellulose	4.5
Renaissance Metal De-Corroder, Picreator Ltd.	Green aqueous solution	Amine complex of hydro-oxycarboxilic acid	c. 4

The inclusion of these proprietary products is based on the types of products available for use in the U.K. for the conservation of historic metal objects, and the conservation preparations are examples of the types of materials used in museums in my experience as an Objects Conservator. Specific questions concerning the use of these proprietary products and conservation preparations in the conservation of metal objects were addressed in the Research MSc. For example examining the difference in the effects of using 5% w/v disodium EDTA in a solution compared with 5% w/v disodium EDTA in a gel, as there is a risk of etching the lead surface when using an EDTA solution for prolonged periods of time, but also a risk of differential aeration corrosion when using gels, if they are allowed to dry out unevenly over the surface being treated (Pearson, 1988). The type of water used in the conservation of lead objects is also a discussion point in the conservation literature, as some references recommend using tap water due to the corrosive effects of pure deionised/distilled water on lead (North, 1987: 244), while other references recommend the use of boiled deionised water, as it is considered non-corrosive (Selwyn, 2004: 119).

General metal cleaning products such as Nevr Dull Wadding Polish and Pre-Lim Surface Cleaner were included to investigate the effects of these types of proprietary products on different metals and demonstrate that they may not be appropriate for all the types of metals suggested in their product information. Goddard's Silver Dip, Liberon Brass and Copper Polish and Renaissance Metal De-Corroder were included to visually document the effects of using acidic proprietary products, while Silvo Silver Polish was included to visually document the effects of using alkaline products containing ammonia. Acidified thiourea solutions such as silver dip are known to lead to preferential corrosion at the grain boundaries in silver alloys with prolonged use, and can cause inter-granular corrosion and pitting in the surface (North, 1980: 44). The use of silver dip can also leave a yellow-brown surface discolouration after treatment, particularly if there are cavities and hollow parts that may be difficult to rinse thoroughly (North, 1980: 45; Selwyn and Costain, 1991: 14; Bishop Museum, 1996). This is the case even if the silver dip solution is applied on cotton swabs, as is now favoured to avoid over cleaning. As a result, cleaning the surface with a silver polishing cloth after using silver dip is often recommended, which is an additional step that removes more silver from the surface (North, 1980: 45). Research carried out by Jannen Contreras on the effects of acidified thiourea solutions such as silver dip on Mexican silver coinage for a MSc in Forensic Heritage Science at the University of Lincoln in 2010-2011 indicated that silver dip may be preferentially corroding the copper component in silver-copper alloys to the extent that the surface becomes enriched with silver (Contreras, 2011).

The use of alkaline metal polishes containing ammonia such as Silvo Silver Polish, Autosol and Brasso is also problematic, as the ammonia in these products can cause uniform corrosion and stress corrosion cracking in metal alloys containing copper (Storch, 2004; Selwyn, 2004: 69). Silvo Silver Polish was therefore included in the study, to see if negative side effects were visible in the ESEM-EDX analysis. In addition, proprietary silver polishes can also contain sulphur based tarnish inhibitors which impart a wax like surface layer that protects the silver from atmospheric pollutants, but they are not recommended as the protective layer can interfere with the application of lacquer coatings, as well as facilitate uneven re-tarnishing of the silver surface (Selwyn, 2004: 139). Alternately the use of precipitated calcium carbonate in a paste with ethanol is thought to be one of the least damaging treatment options for cleaning silver and was included in the ESEM-EDX analysis as a comparison. Precipitated calcium carbonate is recommended rather than levigated calcium carbonate due to the fine particle size, however it is acknowledged that precipitated calcium carbonate can still cause scratching of silver, but the scratches are not visible without magnification (Selwyn, 1999), and this was also investigated in the ESEM-EDX analysis. Renaissance Metal De-Corroder is used in the conservation of iron in the U.K. and was included in the ESEM-EDX analysis to see what the visual effects were on the surface of the iron coupons, as the pH is acidic at c. 4 and the deep green colour of the solution is unusual for chemicals used in conservation treatments. A summary of the proprietary products and conservation preparations analysed and the metals they are used to treat is given in **Table 7.**

Table 7: The proprietary products and conservation preparations and the types of metals they were tested on.

Proprietary Products and Conservation Preparations	**Metal Samples**			
	Silver (Ag)	**Copper (Cu)**	**Lead (Pb)**	**Iron (Fe)**
Goddard's Silver Dip	X			
Silvo Silver Polish	X			
Precipitated Calcium Carbonate Paste in Ethanol	X			
Liberon Brass and Copper Polish		X		
Nevr Dull Wadding Polish		X		X
Pre-Lim Surface Cleaner		X		X
5% w/v disodium EDTA in deionised water			X	
5% w/v disodium EDTA in boiled deionised water			X	
5% w/v disodium EDTA in boiled deionised water made into a gel with 5% w/v methyl cellulose			X	
Renaissance Metal De-Corroder				X

4.4 Analytical Techniques

4.4.1 Portable X-ray Fluorescence Spectroscopy

The elemental analysis of the silver, copper, lead and iron control IV coupons was carried out using the Thermo Scientific Niton XL 3t pXRF analyzer in the Science Faculty at the University of Lincoln, shown in **Figure 9** in section 3.4.1. A discussion of the XRF analytical technique has been given in section 3.4.1 and the operating parameters used in the pXRF analysis of the metal coupons are the same as those discussed in section 3.5.1 for the modern religious medals.

4.4.2 Environmental Scanning Electron Microscopy coupled with Energy Dispersive X- Ray Spectroscopy

The effects of the cleaning treatments on the silver, copper, lead and iron coupons were analysed with the tungsten based FEI Inspect S50 environmental scanning electron microscope coupled with an energy dispersive X-ray spectrometer (ESEM-EDX) in the Science Faculty at the University of Lincoln, shown in **Figure 11** in section 3.4.2. A discussion of this analytical technique has been given in section 3.4.2 and the operating parameters are the same as those discussed in section 3.5.2 for the analysis of the modern religious medals. In this research component however the focus in the ESEM-EDX analyses was to visually document the surface of the metal coupons with ESEM photomicrographs of the same areas at increasing magnifications before and after treatment, and then regularly over a period of six months to examine any residual effects of the treatments. EDX analyses were carried out to provide semi-quantitative information on the elements present on the surface of the coupons each time they were examined at 100x magnification, as well as to check for any residues of the treatments at higher magnifications.

4.5 Experimental

4.5.1 Elemental Characterisation of the Metal Coupons using pXRF

The upper surfaces of the degreased control coupons IV of each type of metal were analysed using the Thermo Scientific Niton XL 3t pXRF analyzer secured in the stationary bench top Thermo Scientific Smart Stand shown in Figures 9, 12 and 13. A discussion of the XRF technique is given in section 3.4.1 of this thesis and the experimental parameters for the pXRF analysis are documented in section 3.5.1. The same operating parameters were used in the pXRF analysis of the metal coupons as the modern religious medals. The pXRF analyzer was regularly calibrated with the integrated reference standards, and the calibration was checked

against a series of metal reference standards. The pXRF results for the internal calibration of the Thermo Scientific Niton XL 3t pXRF analyzer are recorded in **Table 3** in section 3.5.1 and the estimated optimal limits of detection (LODs) for the Thermo Scientific Niton XL 3t pXRF analyzer are given in **Table 1** in section 3.5.1. The pXRF results for the metal reference standards are recorded in **Table 8** below, and include an iron (Fe) reference standard this time, as this was relevant to the pXRF analysis of the effects of treatments used in metals conservation since one of the types of metal coupons tested was an iron alloy. Given that the metal coupons have flat, clean and homogeneous surfaces only three repeat readings were taken to analyse the elemental composition. The pXRF results for control coupons Ag IV, Cu IV and Fe IV are shown in **Table 9.** The pXRF results for control coupon Pb IV are shown in **Table 10,** as minor elements with > 1 wt. % were identified in the lead coupon.

Table 8: pXRF analysis of the copper, silver and iron reference standards supplied by Goodfellow Cambridge Ltd., U.K.

Reference Standard		**Copper 99.95 wt. %**		**Silver 99.9 wt.%**		**Iron 99.5 wt. %**	
Reading #		**Cu wt. %**	**± Cu Error**	**Ag wt. %**	**± Ag Error**	**Fe wt. %**	**± Fe Error**
	1	99.7	0.41	98.8	0.54	99.4	0.32
	2	99.7	0.42	99.2	0.53	99.4	0.30
	3	99.7	0.42	99.1	0.54	99.3	0.32
	4	99.6	0.42	99.1	0.53	99.3	0.32
	5	99.7	0.39	99.1	0.55	99.1	0.31
	6	99.7	0.39	99.1	0.53	99.5	0.31
	7	-	-	99.2	0.22	99.4	0.32
	8	-	-	99.3	0.22	99.4	0.33
	9	-	-	99.3	0.22	99.3	0.28
Mean		99.7		99.1		99.3	
S.D. (s)		0.04		0.14		0.11	
Error (2s)		± 0.08		± 0.28		± 0.23	

Table 9: pXRF results for the silver (Ag) IV, copper (Cu) IV and iron (Fe) IV coupons.

pXRF results	**Ag, Cu and Fe Metal Coupons**					
	Ag IV wt. %	**± Ag Error wt. %**	**Cu IV wt. %**	**± Cu Error wt. %**	**Fe IV wt.%**	**± Fe Error wt. %**
1	99.0	0.509	99.98	0.21	97.5	0.344
2	98.8	0.494	99.97	0.20	97.6	0.347
3	98.9	0.499	99.98	0.20	97.7	0.328
Mean	98.9	0.501	99.98		97.6	0.340
S.D. (s)	0.09		0.006		0.09	
Error (2s)	0.17		0.012		0.18	

Table 10: pXRF results for the lead (Pb) IV coupon.

pXRF results	Pb Metal Coupon					
	Pb IV wt. %	± Pb Error wt. %	P wt. %	± P Error wt. %	Si wt. %	± Si Error wt. %
1	93.9	0.805	2.68	0.11	2.61	0.16
2	94.1	0.790	2.34	0.11	2.65	0.16
3	93.8	0.799	2.73	0.10	2.72	0.16
Mean	93.9		2.58		2.66	
S.D. (s)	0.19		0.21		0.06	
Error (2s)	0.38		0.42		0.12	

4.5.2 ESEM-EDX Analysis of the Metal Coupons

The upper surface of the degreased silver, copper, lead and iron coupons marked I, II and III were analysed using the tungsten based FEI Inspect S50 ESEM-EDX in the Science Faculty at the University of Lincoln, shown in Figure 11. A discussion of the SEM-EDX technique is given in section 3.4.2 of this thesis and the experimental parameters of the ESEM-EDX are documented in section 3.5.2. The metal coupons were secured to aluminium SEM stubs with carbon tape and placed on the circular stage in the ESEM-EDX chamber for analysis. The digital photograph in **Figure 35** shows the metal coupons secured to the SEM stubs before treatment.

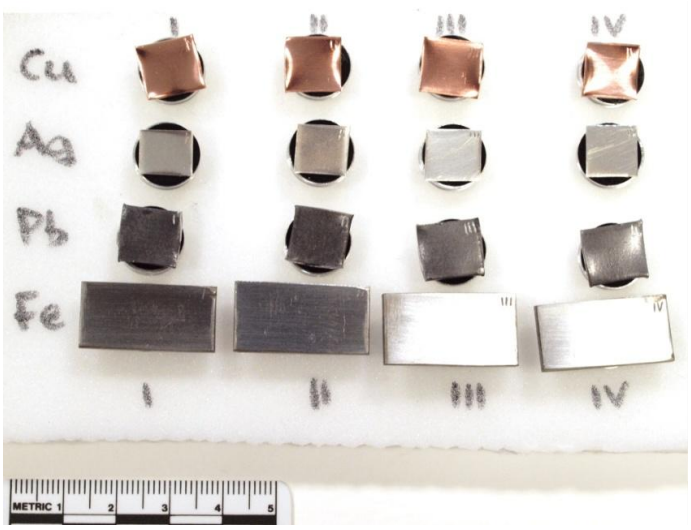


Figure 35: The copper (Cu), silver (Ag), lead (Pb) and iron (Fe) coupons secured on the aluminium SEM stubs with carbon tape before treatment (B.T.).

The ESEM-EDX analyses were carried out under high vacuum at 20 kV with a spot size of 6.0, a working distance of c.10 mm, 60-100 µS dwell time and a resolution of 1024 x 884. ESEM photomicrographs were taken at magnifications of c. 40x, 100x, 500x and 1000x before and after treatment and at two, four and six months after treatment, to record the surface of the

metal coupons and assess the effects of the different treatments over time. The EDX analyses were carried out with an acquisition time of 60 seconds at 100x and higher magnifications where appropriate for each of the metal coupons before and after treatment, and at two, four and six months after treatment to provide semi-quantitative information on the elemental composition and indicate any changes in the metal surfaces. Where ever possible the same area of the metal coupon was analysed each time, using the engraved I, II, III and IV marks in the lower right corner of the ESEM images as a guide. As the magnification increased, distinctive marks such as scratches and imperfections in the surface of the metal coupons were used to locate the same area for analysis. ESEM-EDX analysis of the control coupon IV for each type of metal was also carried out with the same operating parameters and at the same series of magnifications after two, four and six months, as a reference for the changes over time of the untreated metal coupons. The systematic analysis of the bare metal coupons using exactly the same experimental procedure and series of magnifications before and after treatment, then regularly over time for a six month period was also carried out to see if there were any inconsistencies in the ESEM-EDX imaging and the EDX analysis, as this can be a limitation in ESEM-EDX analyses.

The silver, copper, lead and iron coupons marked I, II and III were treated with three different chemical and abrasive proprietary products and conservation preparations in the following order, with the control coupon IV of each type of metal left untreated:

Ag I: Goddard's Silver Dip
Ag II: Silvo Silver Polish
Ag III: Precipitated calcium carbonate in a paste with ethanol
Ag IV Control

Cu I: Liberon Brass and Copper polish
Cu II: Nevr Dull Wadding Polish
Cu III: Pre-Lim Surface Cleaner
Cu IV Control

Pb I: 5 % w/v disodium EDTA in deionised water
Pb II: 5% w/v disodium EDTA in boiled deionised water
Pb III: 5% w/v disodium EDTA in boiled deionised water made into a gel with 5 % w/v methyl cellulose
Pb IV Control

Fe I: Renaissance Metal De-Corroder

Fe II: Pre-Lim Surface Cleaner

Fe III: Nevr Dull Wadding Polish

Fe IV Control

The treatments were carried out with 10-30x magnification using a Meiji EMT stereo microscope and the proprietary products and preparations were systematically applied on cotton swabs 50 times across the surface of the metal coupons. The coupons were left for 30 minutes with the chemical solutions and abrasive materials on the surface before being rinsed with the appropriate solvent or deionised water/boiled deionised water and dewatered with acetone. The metal coupons were then air dried and this process was repeated so that the total time the metal surfaces were in contact with the proprietary products and conservation preparations was one hour. This was carried out to indicate what can happen to the clean metal surface for the different types of metals when there is prolonged contact with the chemical solutions and abrasive materials, as can occur in the treatment of metal objects which are not entirely covered in corrosion products, or if the materials used to treat the metal objects are not completely removed during the rinsing stage and residues remain (Selwyn and Costain, 1991: 6). In addition, the Pb III coupon treated with 5 % w/v disodium EDTA in boiled deionised water in a gel was not covered during treatment to investigate the effects of the uneven drying of the gel on the lead surface and the possibility of differential aeration corrosion occurring, as gels are not always covered when they are used to treat objects, in particular large and awkwardly shaped objects. After treatment, the metal coupons were stored on the SEM stubs in a sealed, inert polypropylene container in ambient laboratory conditions. The photograph in **Figure 36** shows the metal coupons secured to the aluminium SEM stubs after treatment.

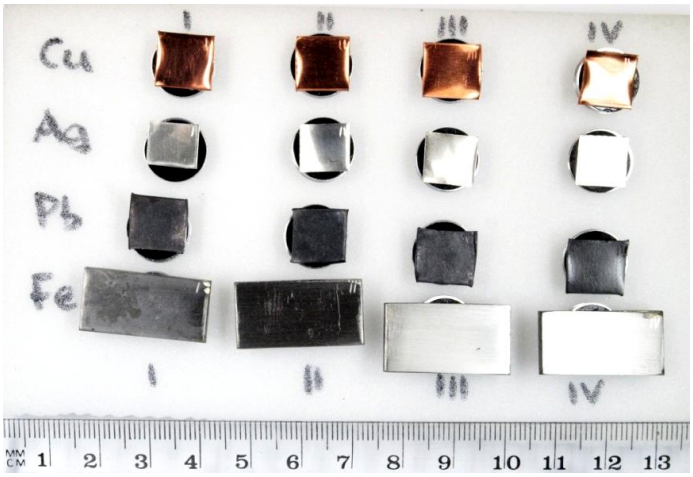


Figure 36: The copper (Cu), silver (Ag), lead (Pb) and iron (Fe) coupons secured on the aluminium SEM stubs with carbon tape after treatment (A.T.).

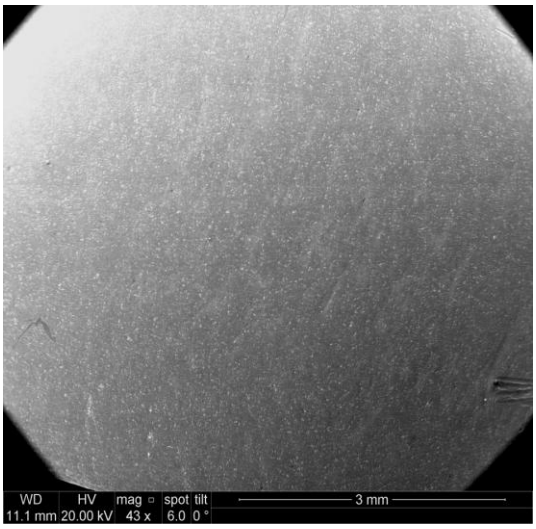
4.6 Results and Discussion

4.6.1 Silver Coupons

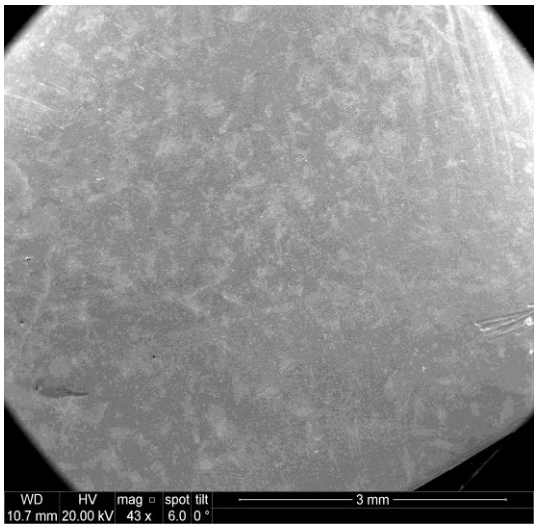
Ag I:

The ESEM photomicrographs of Ag I before and after treatment with Goddard's Silver Dip at magnifications of c. 40x, 100x, 500x and 1000x are shown below, and indicate that the surface of the Ag I coupon was patchy after treatment. This suggests that the silver dip, which has a pH of < 2, etched the silver surface. The patchy surface is visible at a magnification of 40x, which indicates that the types of microscopes commonly found in conservation laboratories and training programmes with magnifications up to c. 60-70x could be useful for examining the effects of chemical treatments such as this. However at the higher magnifications of c. 500x and 1000x dark coloured spots were visible on the surface of the silver coupon, which were not apparent at the lower magnifications.

Figure 37: ESEM-EDX photomicrographs of sample Ag I before and after treatment with Goddard's Silver Dip at magnifications of c. 40x, 100x, 500x and 1000x.

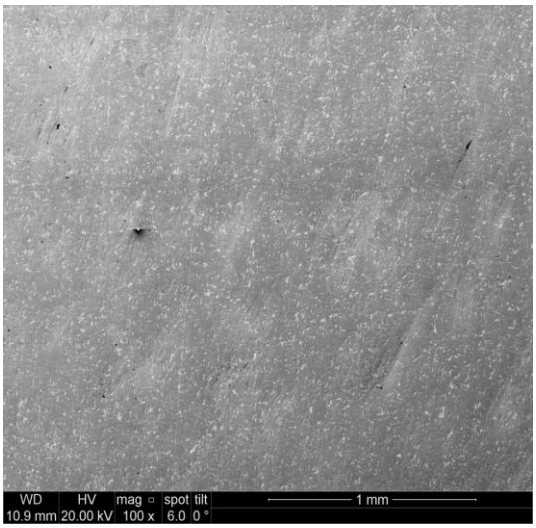


Before treatment at 43x

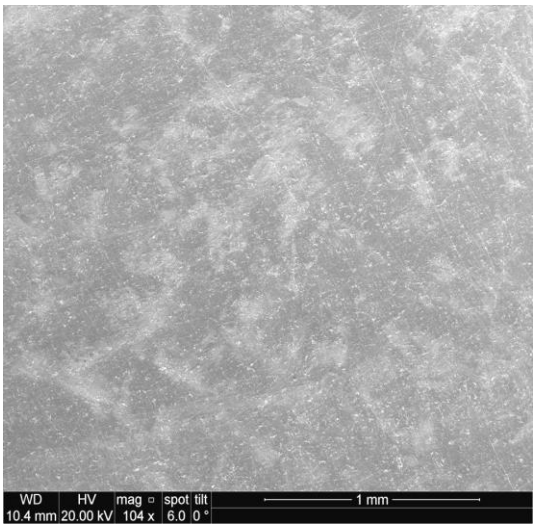


After treatment at 43x

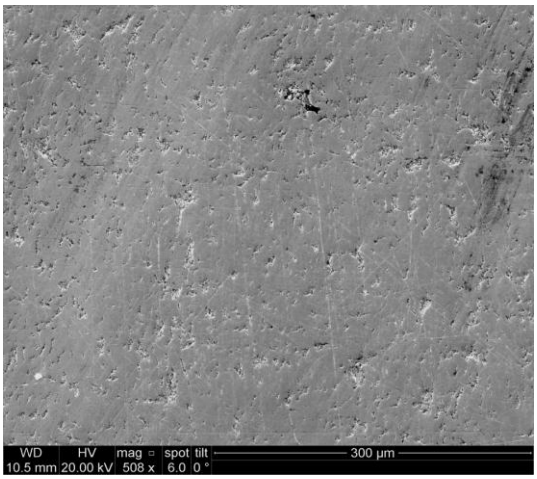
Figure 37 continued: ESEM-EDX photomicrographs of sample Ag I before and after treatment with Goddard's Silver Dip at magnifications of c. 40x, 100x, 500x and 1000x.



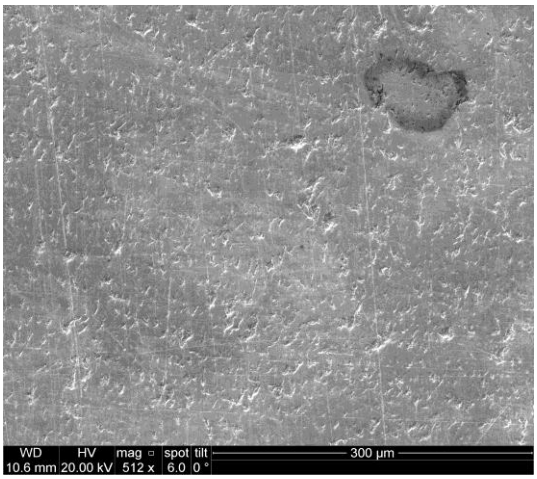
Before treatment at 100x



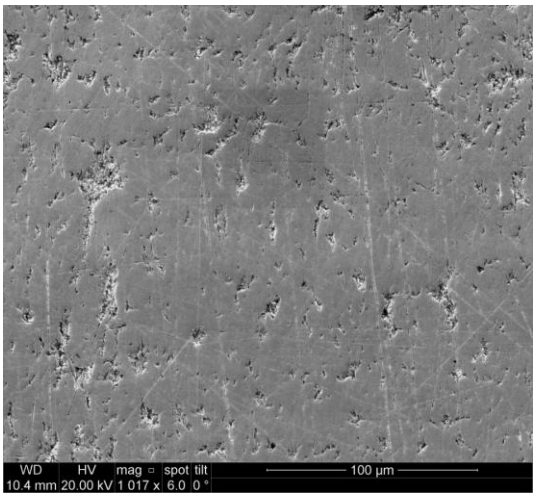
After treatment at 104x



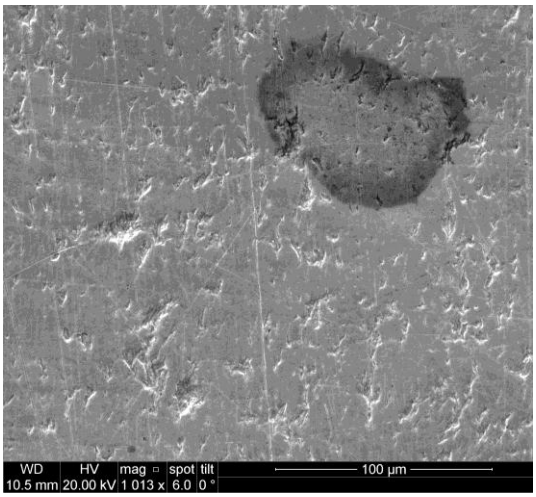
Before treatment at 508x



After treatment at 512x

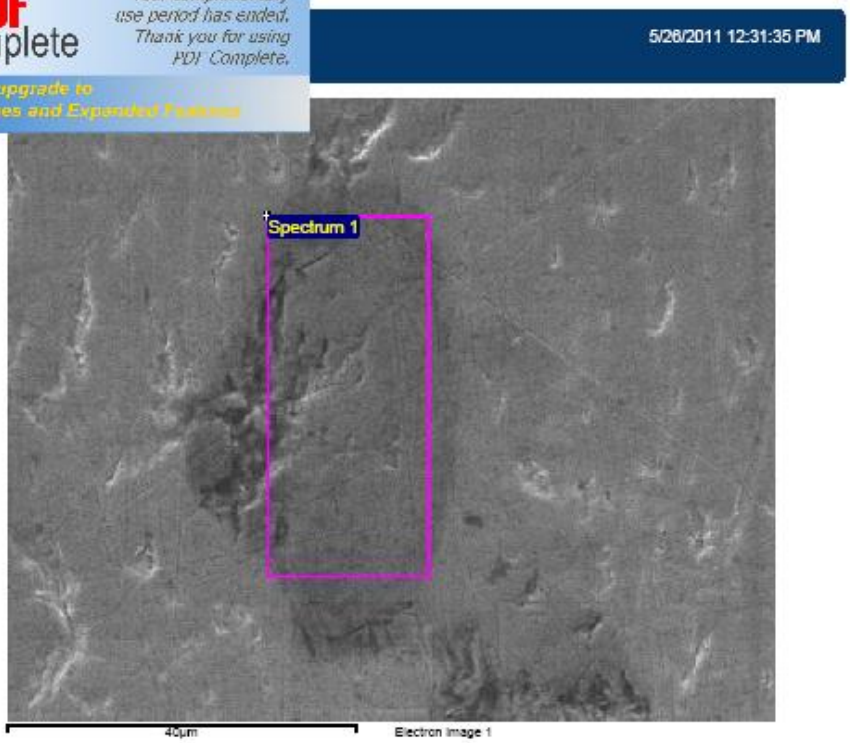


Before treatment at 1017x



After treatment at 1013x

The surface of the Ag I coupon appeared less patchy over time at two, four and six months at lower magnifications of c. 40x and 100x, but there were more dark coloured spots and stains were visible at higher magnifications of c. 500x and 1000x, suggesting that the silver dip had left the silver surface reactive. The EDX analysis of one of these dark spots was carried out at 3062x magnification and the results are shown in **Figure 38**. Silver and carbon were identified, which is consistent with the EDX analyses of the silver control coupon IV, therefore analysis with techniques that identify inorganic and organic materials could be useful such as FTIR micro-spectroscopy or Raman spectroscopy. There was also a yellow-brown discolouration to the surface of the Ag I soon after treatment, which was visible without magnification. This discolouration has been reported in the conservation literature on the use of silver dip (North, 1980: 45; Selwyn and Costain, 1991:14; Bishop Museum, 1996). The ESEM photomicrographs of the Ag I coupon at two, four and six months after treatment at c. 40x, 100x, 500x and 1000x are shown after the EDX analysis results in Figure 37 and they demonstrate the relative consistency in the ESEM images. This was the case with all the ESEM images for the metal coupons analysed after treatments at two, four and six months and they are also included in the text to show the consistency in the ESEM results.



Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	Ag	Total
Spectrum 1	Yes	3.29	96.71	100.00
Mean		3.29	96.71	100.00
Std. deviation		0.00	0.00	
Max.		3.29	96.71	
Min.		3.29	96.71	

All results in weight%

INCA

Figure 38: EDX results for the dark spot on the surface of Ag I after treatment with Goddard's Silver Dip at 3062x.

Figure 39: ESEM-EDX photomicrographs of sample Ag I two months after treatment with Goddard's Silver Dip at magnifications of 41x (a), 100x (b), 509x (c) and 1012x (d).

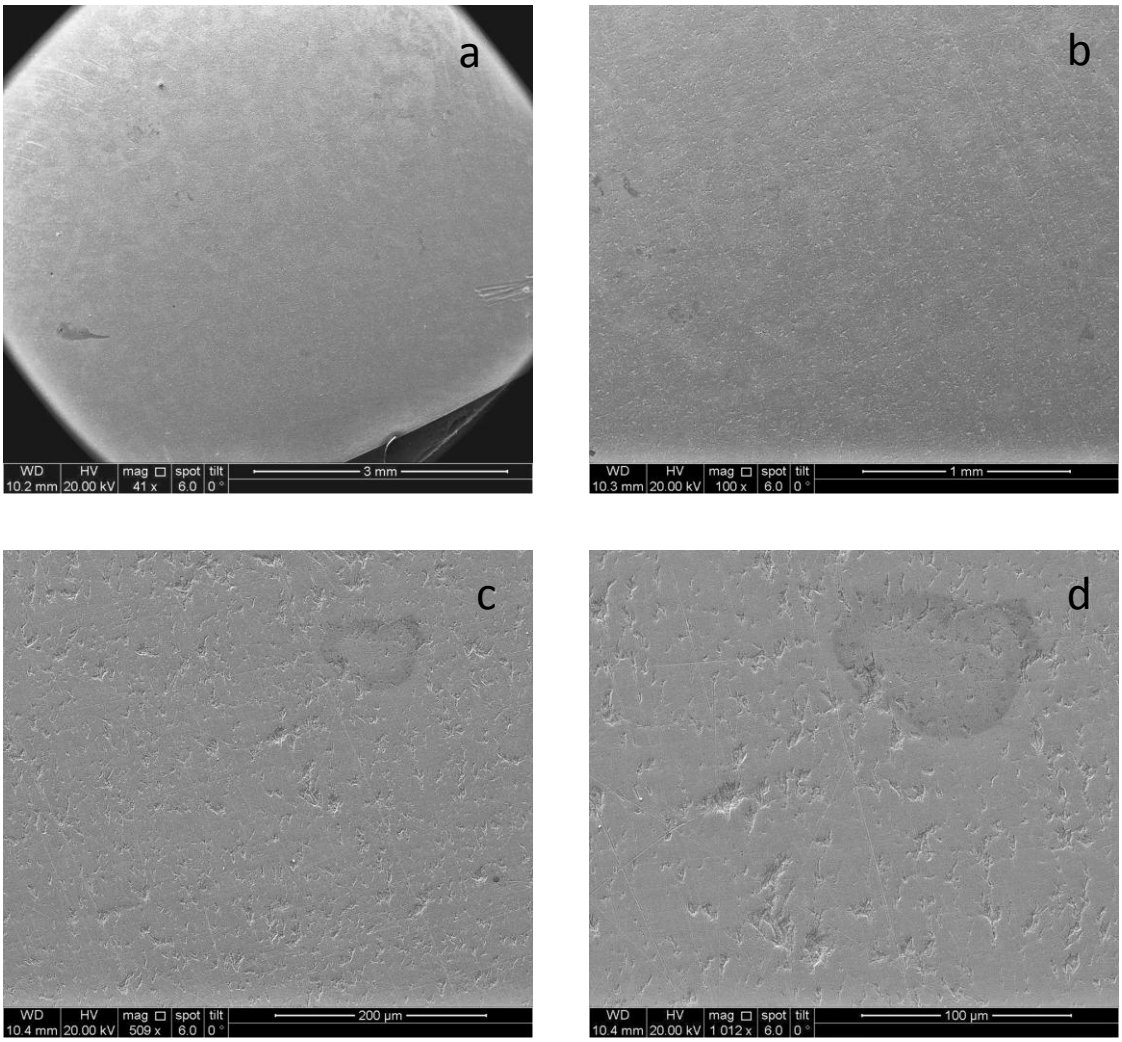


Figure 40: ESEM-EDX photomicrographs of sample Ag I four months after treatment with Goddard's Silver Dip at magnifications of 43x (a), 100x (b), 515x (c) and 1030x (d).

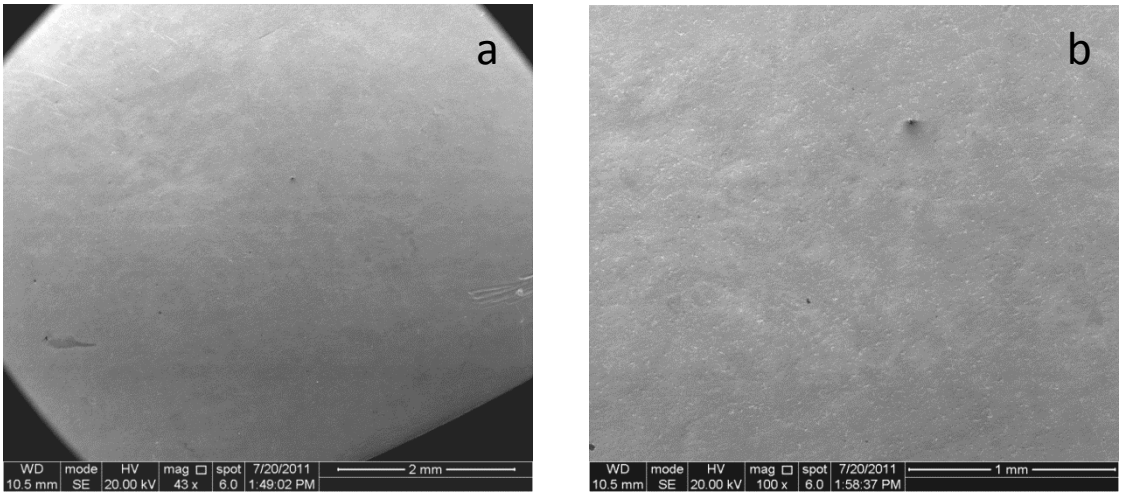


Figure 40 continued: ESEM-EDX photomicrographs of sample Ag I four months after treatment with Goddard's Silver Dip at magnifications of 43x (a), 100x (b), 515x (c) and 1030x (d).

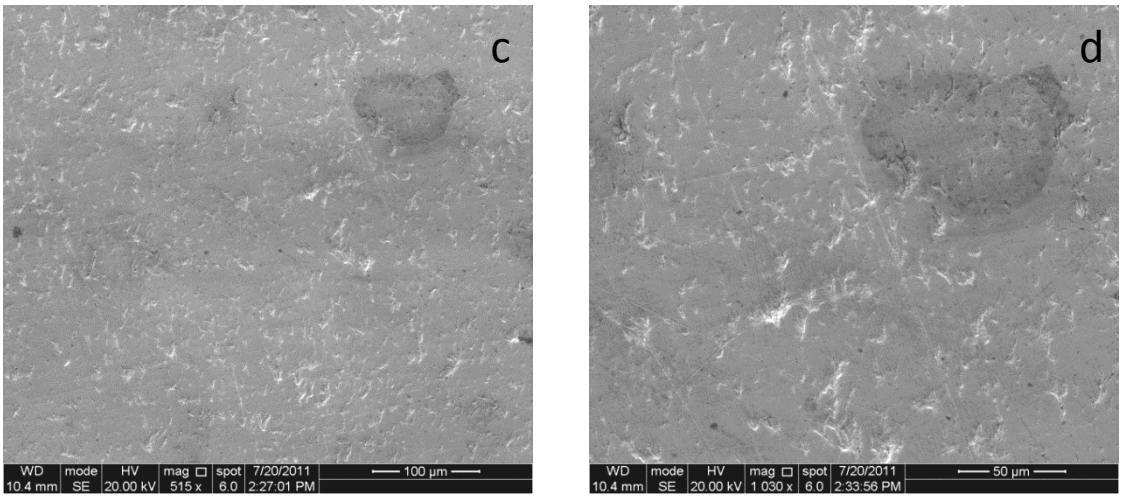
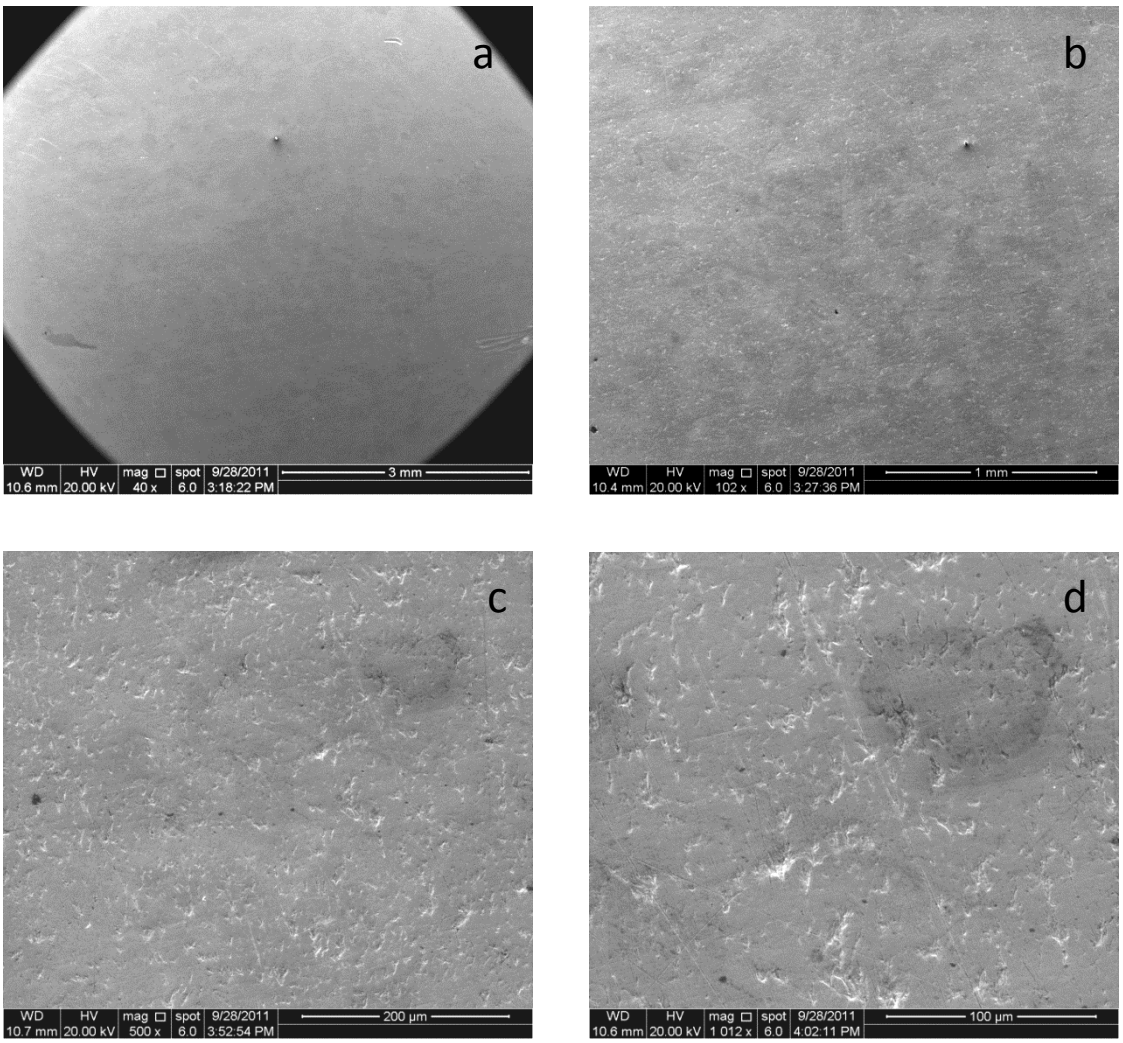


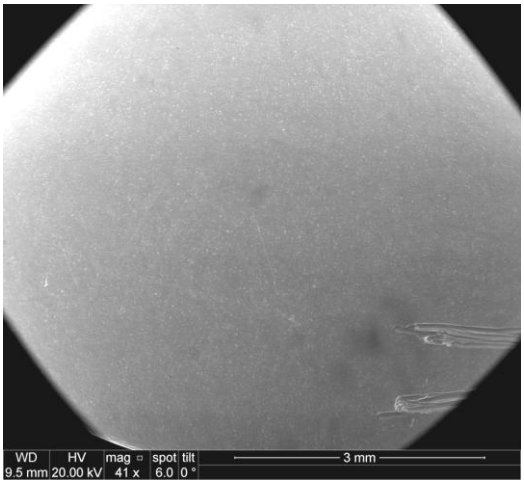
Figure 41: ESEM-EDX photomicrographs of sample Ag I six months after treatment with Goddard's Silver Dip at magnifications of 40x (a), 102x (b), 500x (c) and 1012x (d).



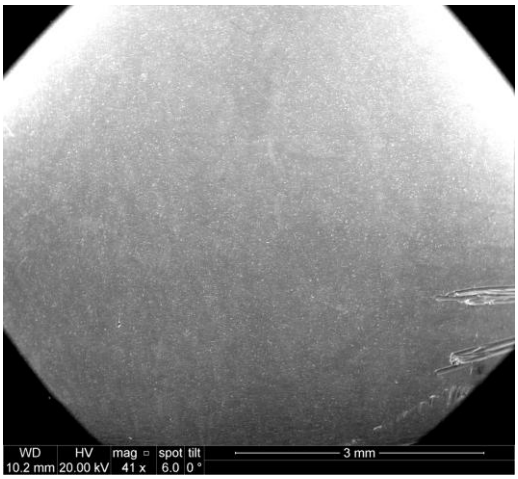
Ag II:

The ESEM photomicrographs of Ag II before and after treatment with Silvo Silver Polish at magnifications of c. 40x, 100x, 500x and 1000x are shown below. The surface of the Ag II coupon appeared to be slightly patchy after treatment at the lower magnifications of 40x and 100x, while at the higher magnifications of c. 500x and 1000x numerous small dark spots were visible, suggesting that there may be fine pitting in the surface. This is consistent with the conservation literature as Silvo contains ammonium hydroxide and products containing ammonia are known to cause corrosion (Storch, 2004; Selwyn, 2004:69). There also appeared to be slightly more scratches in the silver surface after treatment at the higher magnifications. The scratching is not surprising given that Silvo contains quartz as an abrasive which has a hardness of 7 on the Mohs hardness scale, whereas silver has a hardness of 2.5-4 (Ted Pella, 2013).

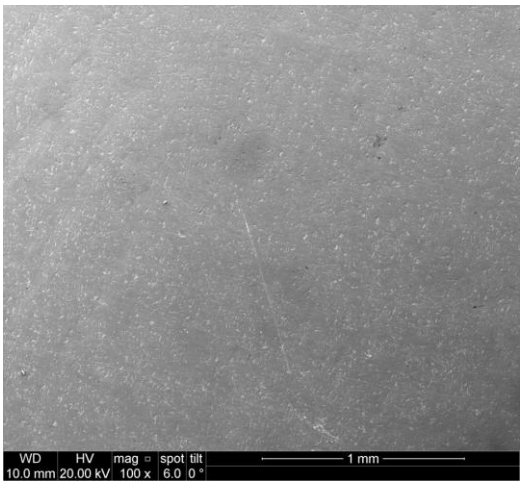
Figure 42: ESEM-EDX photomicrographs of sample Ag II before and after treatment with Silvo Silver Polish at magnifications of c. 40x, 100x, 500x and 1000x.



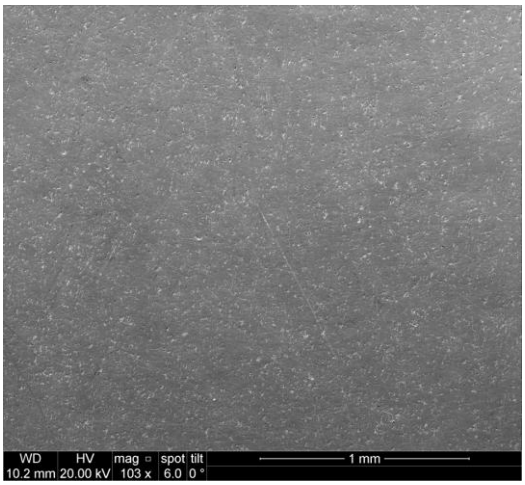
Before treatment at 41x



After treatment at 41x

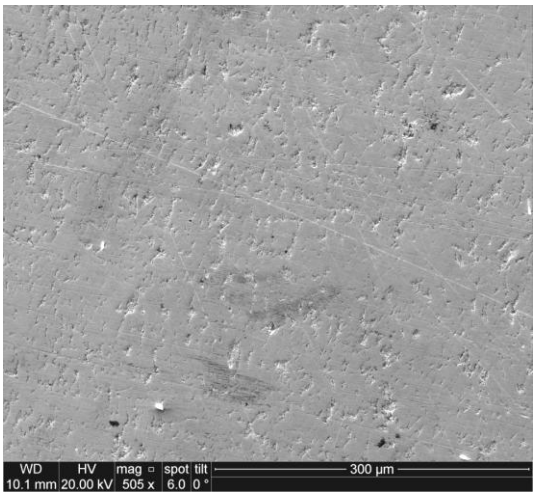


Before treatment at 100x

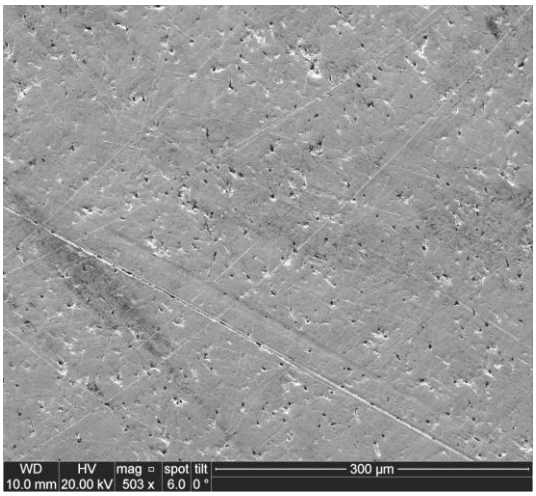


After treatment at 103x

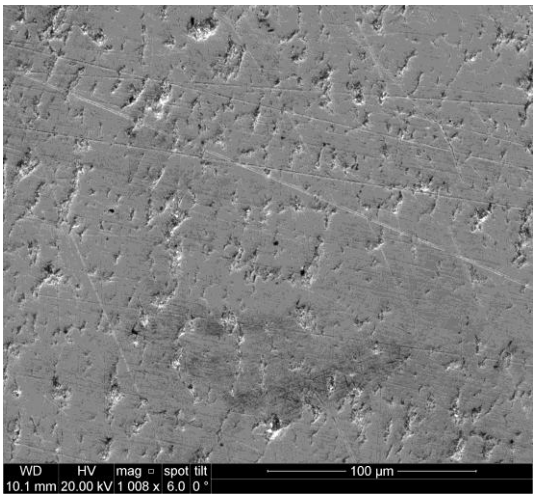
Figure 42 continued: ESEM-EDX photomicrographs of sample Ag II before and after treatment with Silvo Silver Polish at magnifications of c. 40x, 100x, 500x and 1000x.



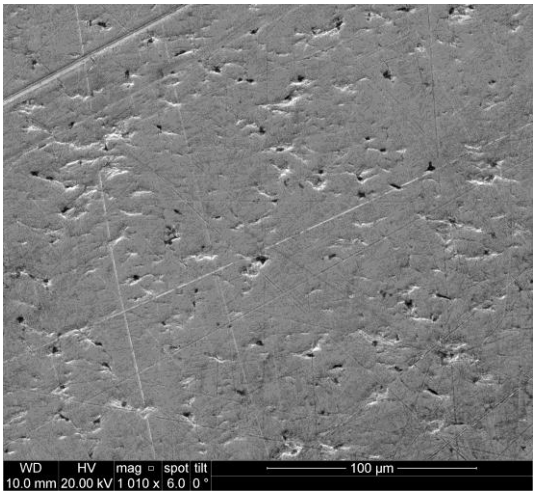
Before treatment at 505x



After treatment at 503x



Before treatment at 1008x



After treatment at 1010x

The surface of the Ag II coupon was less patchy over time at two, four and six months, but the small dark spots which suggested fine surface pitting remained. There was also a yellow-brown discolouration visible after two months without magnification. This suggests that the silver surface was reactive and tarnishing. The ESEM photomicrographs of the Ag II coupon after two, four and months at c. 40x, 100x and 500x and 1000x are as follows:

Figure 43: ESEM-EDX photomicrographs of sample Ag II two months after treatment with Silvo Silver Polish at magnifications of 40x (a), 104x (b), 502x (c) and 1007x (d).

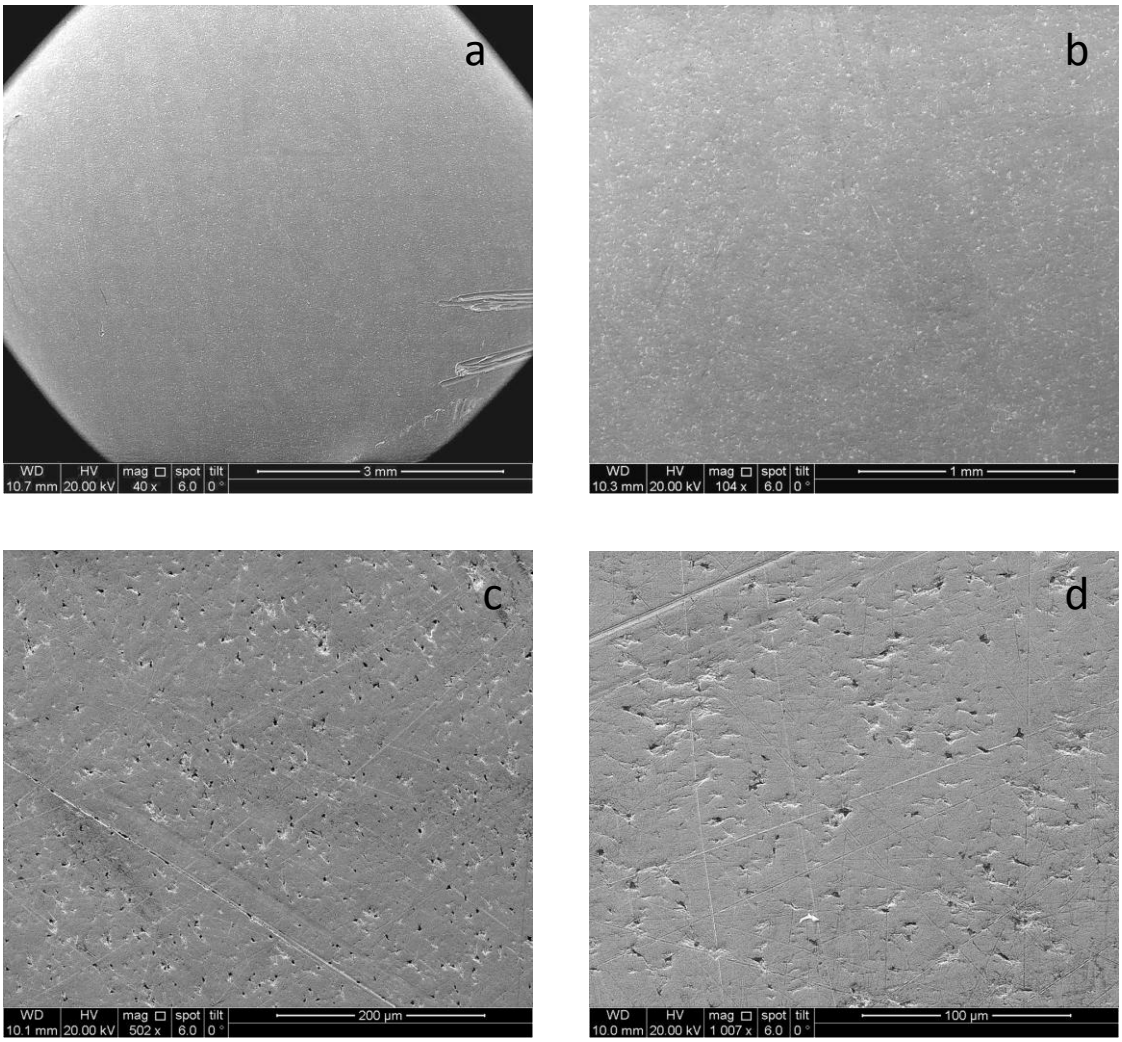


Figure 44: ESEM-EDX photomicrographs of sample Ag II four months after treatment with Silvo Silver Polish at magnifications of 40x (a), 100x (b), 508x (c) and 1001x (d).

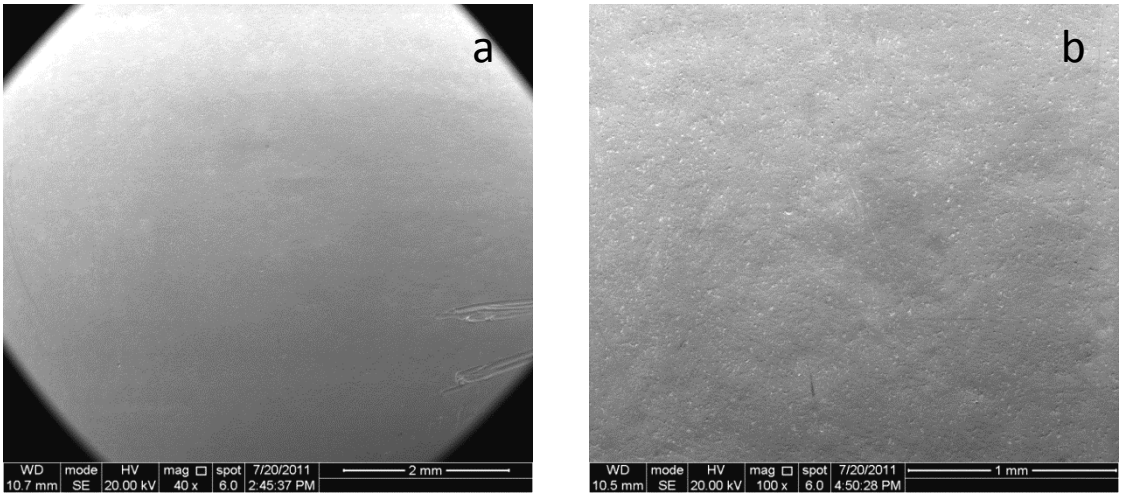


Figure 44 continued: ESEM-EDX photomicrographs of sample Ag II four months after treatment with Silvo Silver Polish at magnifications of 40x (a), 100x (b), 508x (c) and 1001x (d).

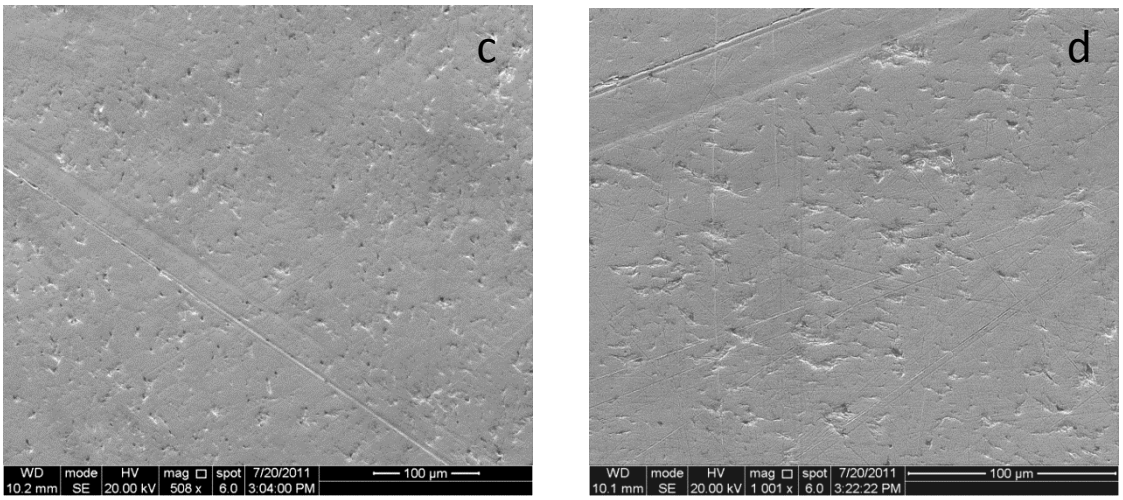
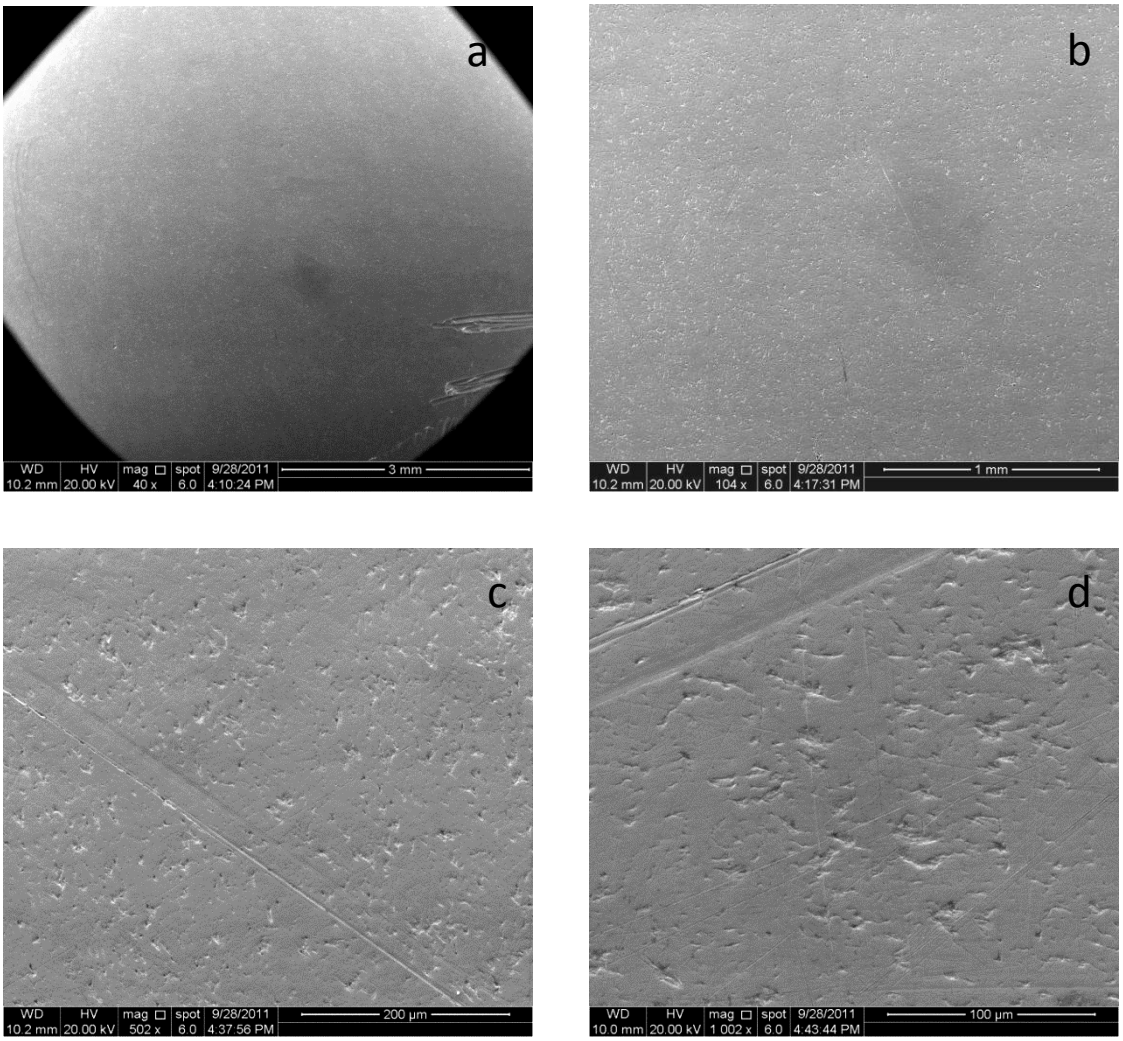


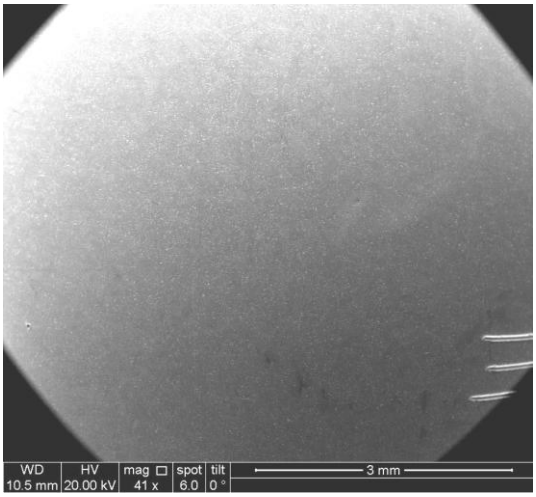
Figure 45: ESEM-EDX photomicrographs of sample Ag II six months after treatment with Silvo Silver Polish at magnifications of 40x (a), 104x (b), 502x (c) and 1002x (d).



Ag III:

The ESEM photomicrographs of Ag III before and after treatment with precipitated calcium carbonate in a paste with ethanol at magnifications of c. 40x, 100x, 500x and 1000x are shown below. The Ag III coupon appeared to be relatively unchanged after treatment, though the surface appeared slightly more uneven after treatment at c. 100x magnification. This was not visible at the higher magnifications of c. 500x and 1000x, however fine scratches were visible, which is consistent with the conservation literature, as calcium carbonate has a hardness of 3 on the Mohs hardness scale while silver/silver alloys have a hardness of 2.5-4 (Ted Pella Inc, 2013). Despite this, the surface of the Ag III coupon after treatment showed the least changes of the three silver coupons, in that it was the least scratched and uneven. The surface appeared cleaner and no residues of the calcium carbonate were indicated by the EDX analysis at 100x after treatment. N.B.: Due to technical problems with the software for the ESEM-EDX, there was a delay before the after treatment ESEM photomicrographs could be taken.

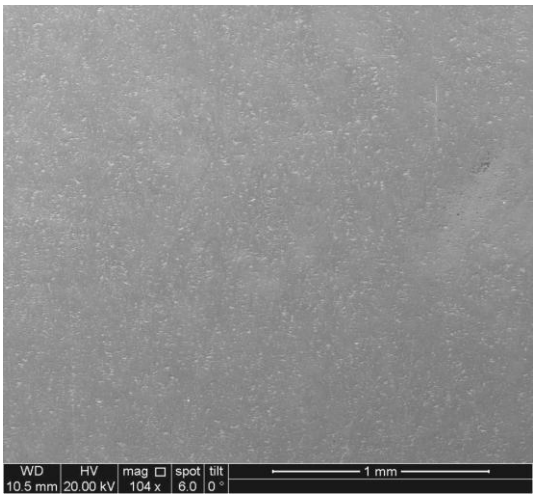
Figure 46: ESEM-EDX photomicrographs of sample Ag III before and after treatment with precipitated calcium carbonate in a paste with ethanol at magnifications of c. 40x, 100x, 500x and 1000x.



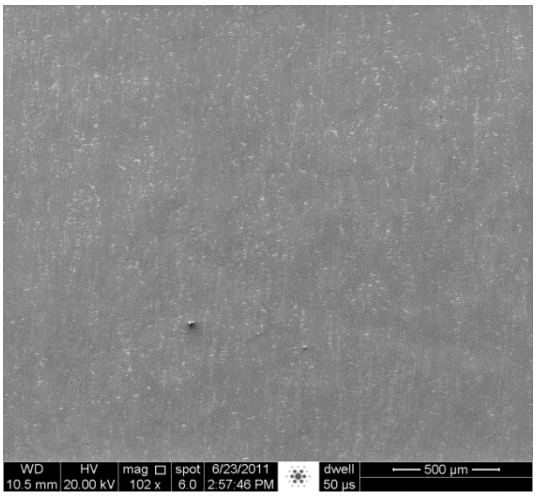
Before treatment at 41x

After treatment at 40x

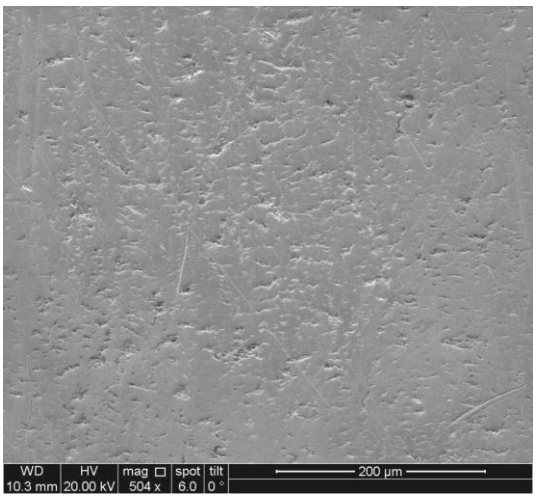
Figure 46 continued: ESEM-EDX photomicrographs of sample Ag III before and after treatment with precipitated calcium carbonate in a paste with ethanol at magnifications of c. 40x, 100x, 500x and 1000x.



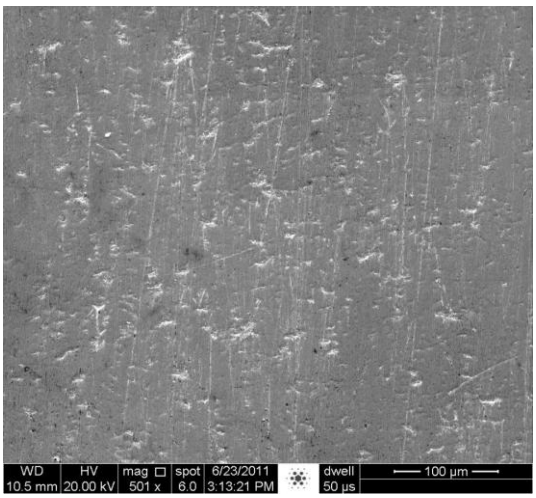
Before treatment at 104x



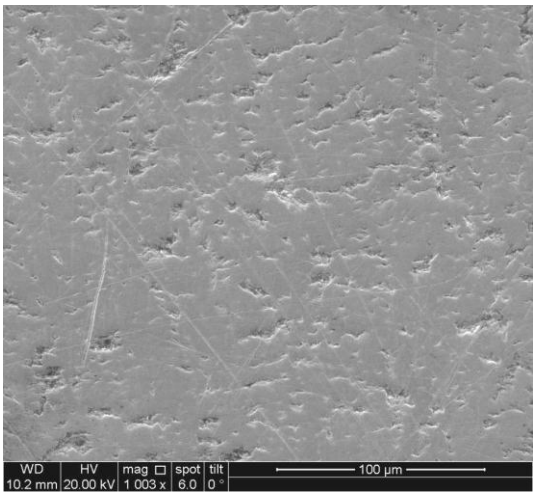
After treatment at 102x



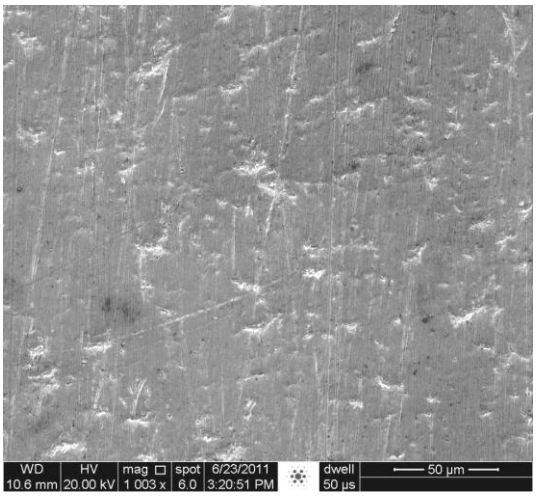
Before treatment at 504x



After treatment at 501x



Before treatment at 1003x



After treatment at 1003x

The surface of the Ag III coupon remained unchanged over time at two, four and six months, and there was no yellow-brown discolouration visible. The surface still appeared slightly uneven at c. 100x magnifications and the fine scratches were visible at the higher magnifications. However the results suggest that the silver surface was less reactive after treatment with this relatively mild abrasive than the other two Ag coupons which were treated with proprietary products containing highly acidic and alkaline components. The ESEM photomicrographs of the Ag III coupon after two, four and six months at c. 40x, 100x, 500x and 1000x are as follows:

Figure 47: ESEM-EDX photomicrographs of sample Ag III two months after treatment with precipitated calcium carbonate in a paste with ethanol at magnifications of 41x (a), 101x (b), 505x (c) and 1010x (d).

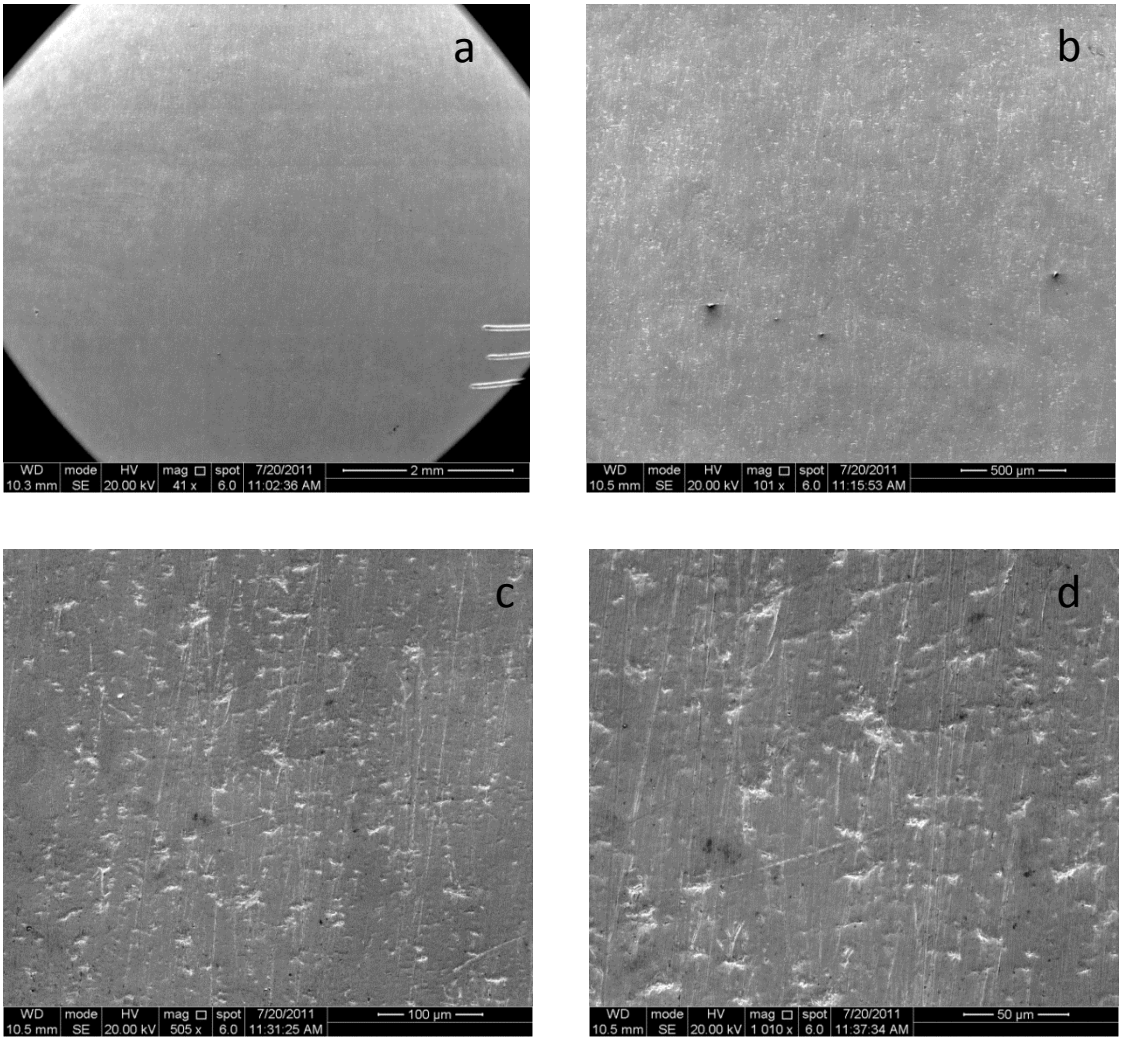


Figure 48: ESEM-EDX photomicrographs of sample Ag III four months after treatment with precipitated calcium carbonate in a paste with ethanol at magnifications of 40x (a), 101x (b), 502x (c) and 1005x (d).

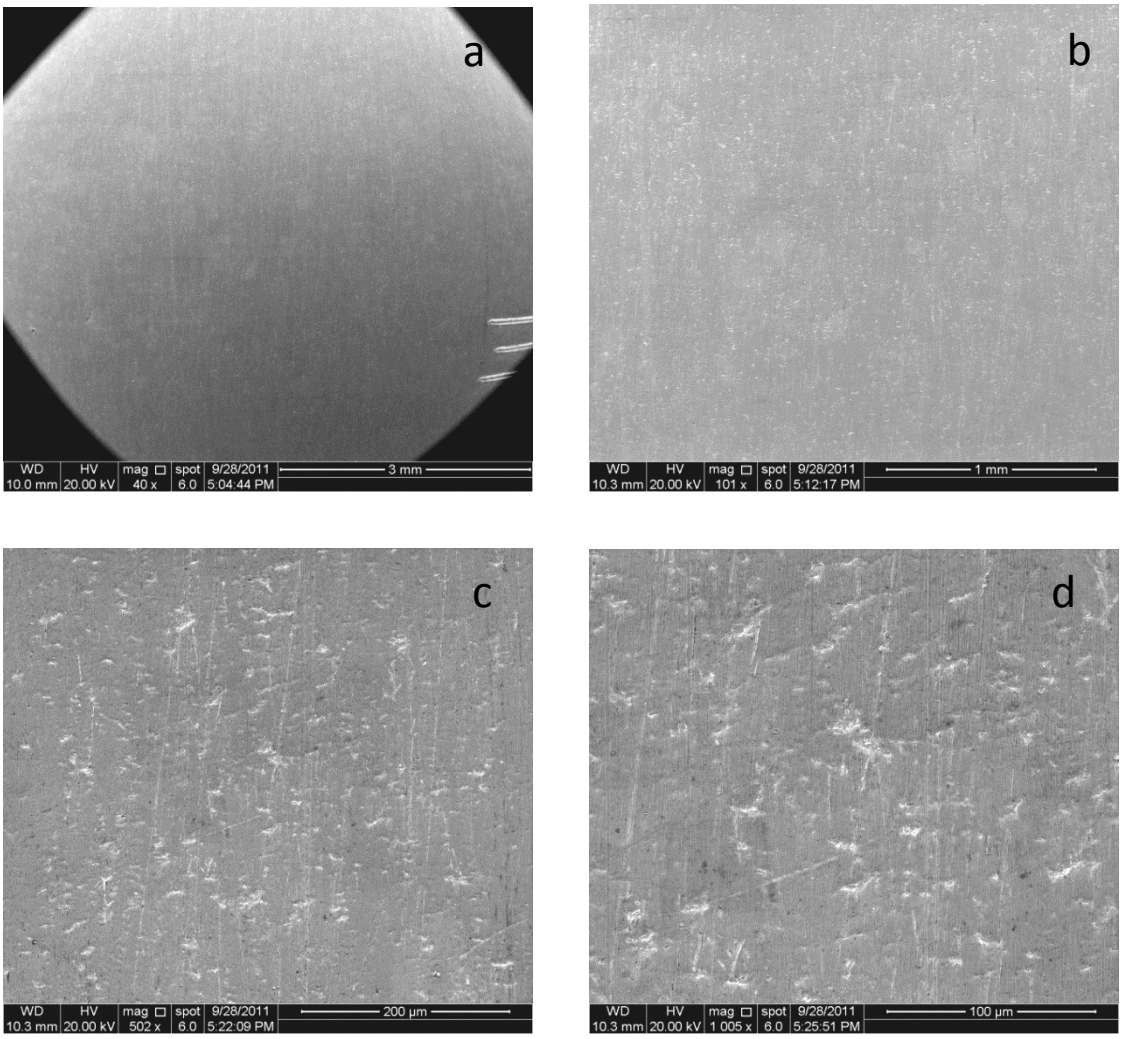


Figure 49: ESEM-EDX photomicrographs of sample Ag III six months after treatment with precipitated calcium carbonate in a paste with ethanol at magnifications of 40x (a), 102x (b), 502x (c) and 1010x (d).

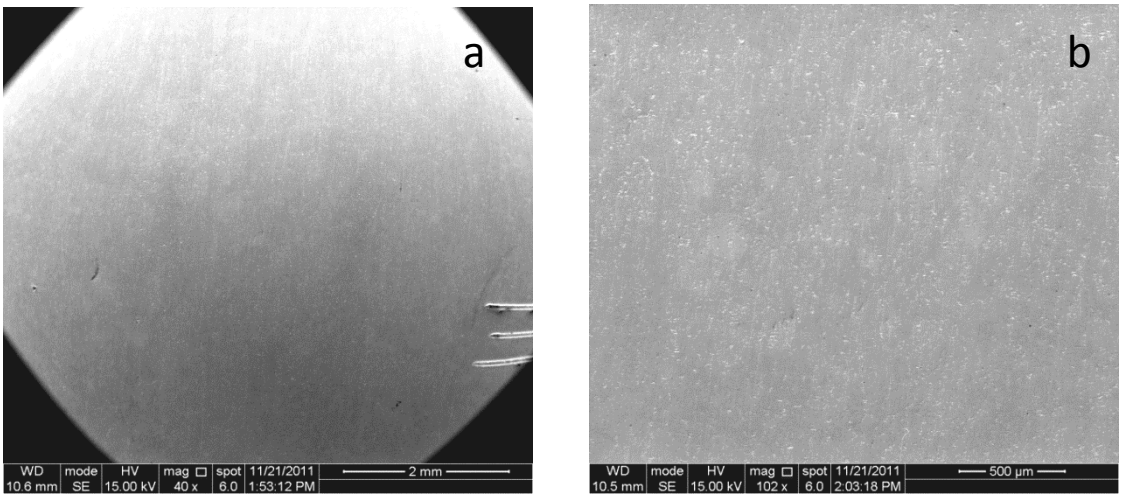
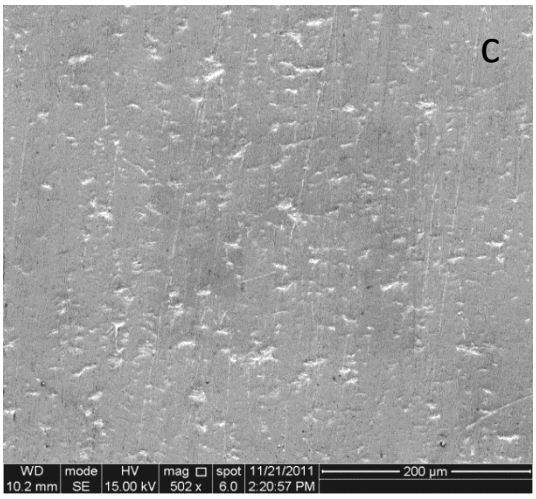
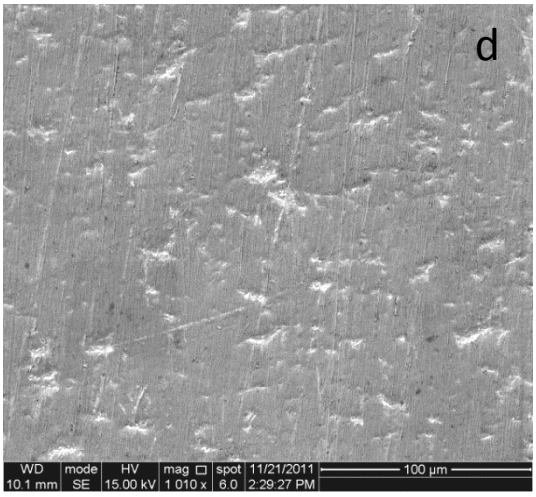


Figure 49 continued: ESEM-EDX photomicrographs of sample Ag III six months after treatment with precipitated calcium carbonate in a paste with ethanol at magnifications of 40x (a), 102x (b), 502x (c) and 1010x (d).



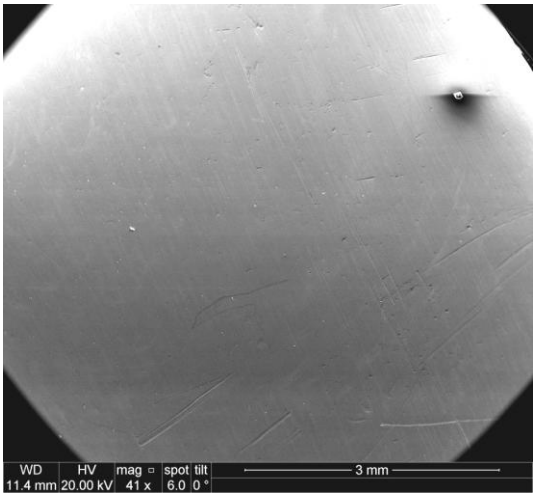


4.6.2 Copper Coupons

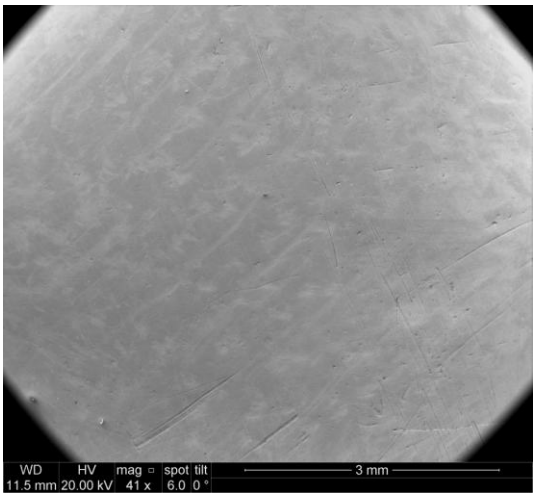
Cu I:

The ESEM photomicrographs of Cu I before and after treatment with Liberon Brass and Copper Polish at magnifications of c. 40x, 100x, 500x and 1000x are shown below. The surface of the Cu I coupon appeared to be patchy after treatment, suggesting that the copper had been etched. There was also considerable scratching in the surface after treatment, visible at the higher magnifications of c. 500x and 1000x. These results are not surprising given that the Liberon Brass and Copper Polish has a pH of 2.4 and contains quartz as an abrasive, which has a hardness of 7 on the Mohs hardness scale, whereas copper has a hardness of 2.5-3 (Ted Pella Inc, 2013).

Figure 50: ESEM-EDX photomicrographs of sample Cu I before and after treatment with Liberon Brass and Copper Polish at magnifications of c. 40x, 100x, 500x and 1000x.

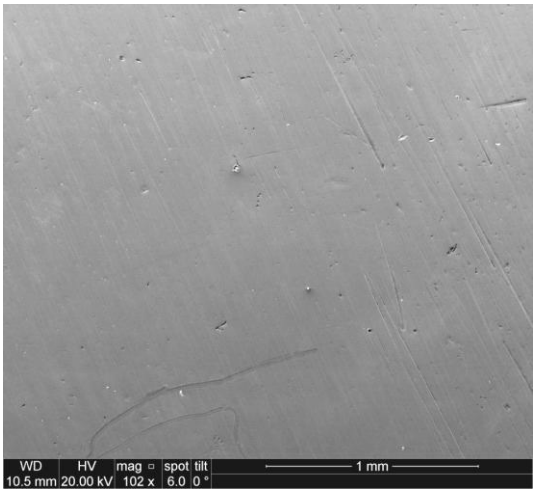


Before treatment at 41x

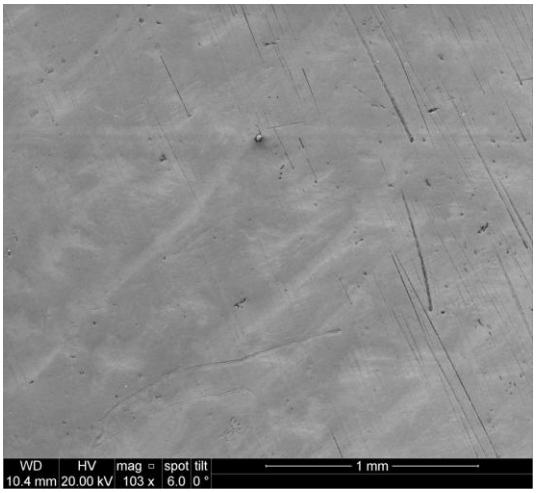


After treatment at 41x

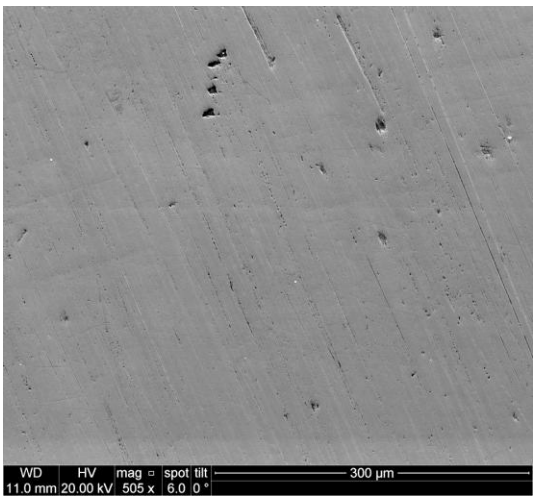
Figure 50 continued: ESEM-EDX photomicrographs of sample Cu I before and after treatment with Liberon Brass and Copper Polish at magnifications of c. 40x, 100x, 500x and 1000x.



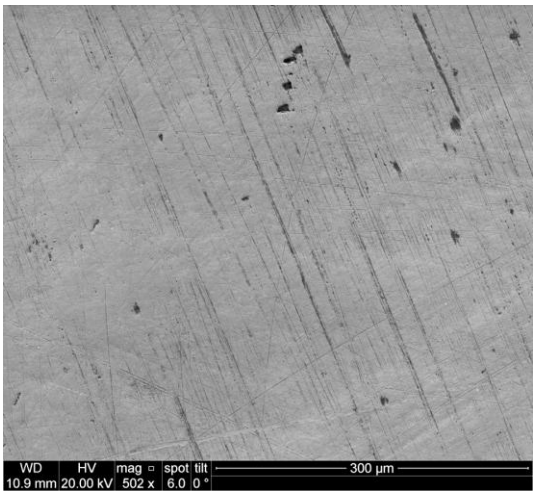
Before treatment at 102x



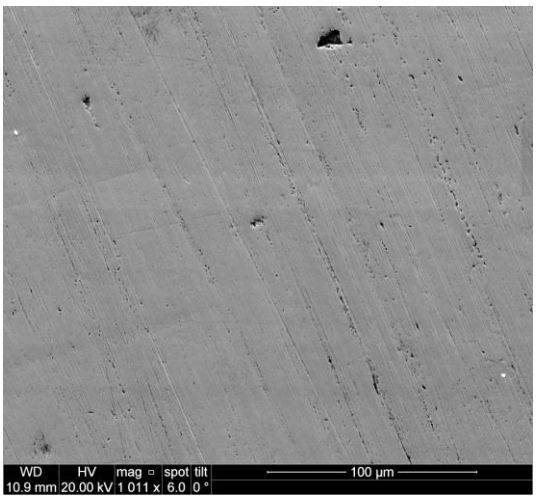
After treatment at 103x



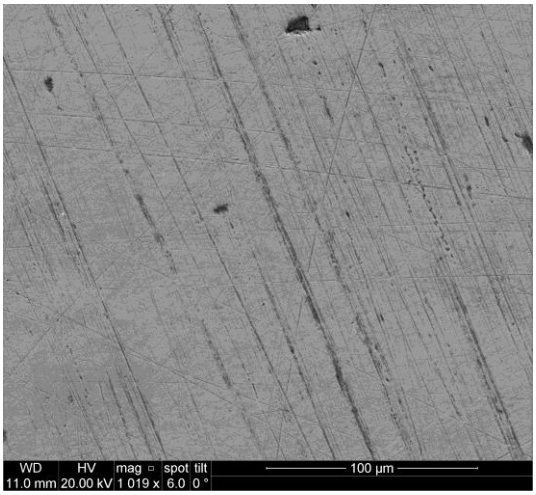
Before treatment at 505x



After treatment 502x



Before treatment at 1011x



After treatment at 1019x

The surface of the Cu I coupon remained patchy at two, four and six months after treatment. This was clearer at magnifications of c. 40x and 100x. While at the higher magnifications of c. 500x and 1000x the scratching in the surface was still visible. The ESEM photomicrographs of the Cu I coupon after two, four and six months at c. 40x, 100x, 500x and 1000x are as follows:

Figure 51: ESEM-EDX photomicrographs of sample Cu I two months after treatment with Liberon Brass and Copper Polish at magnifications of 40x (a), 103x (b), 510x (c) and 1022x (d).

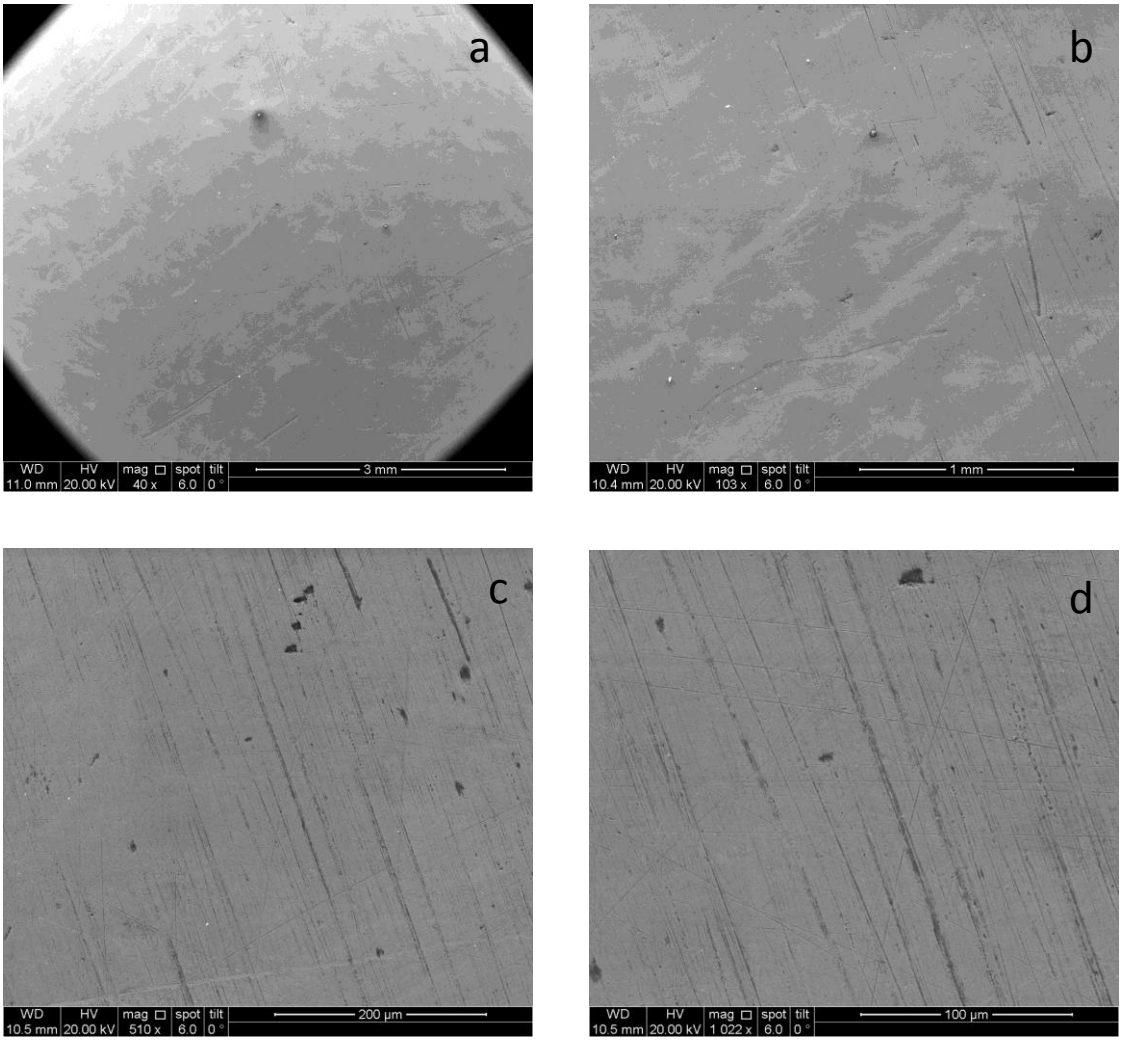


Figure 52: ESEM-EDX photomicrographs of sample Cu I four months after treatment with Liberon Brass and Copper Polish at magnifications of 41x (a), 103x (b), 509x (c) and 1019x (d).

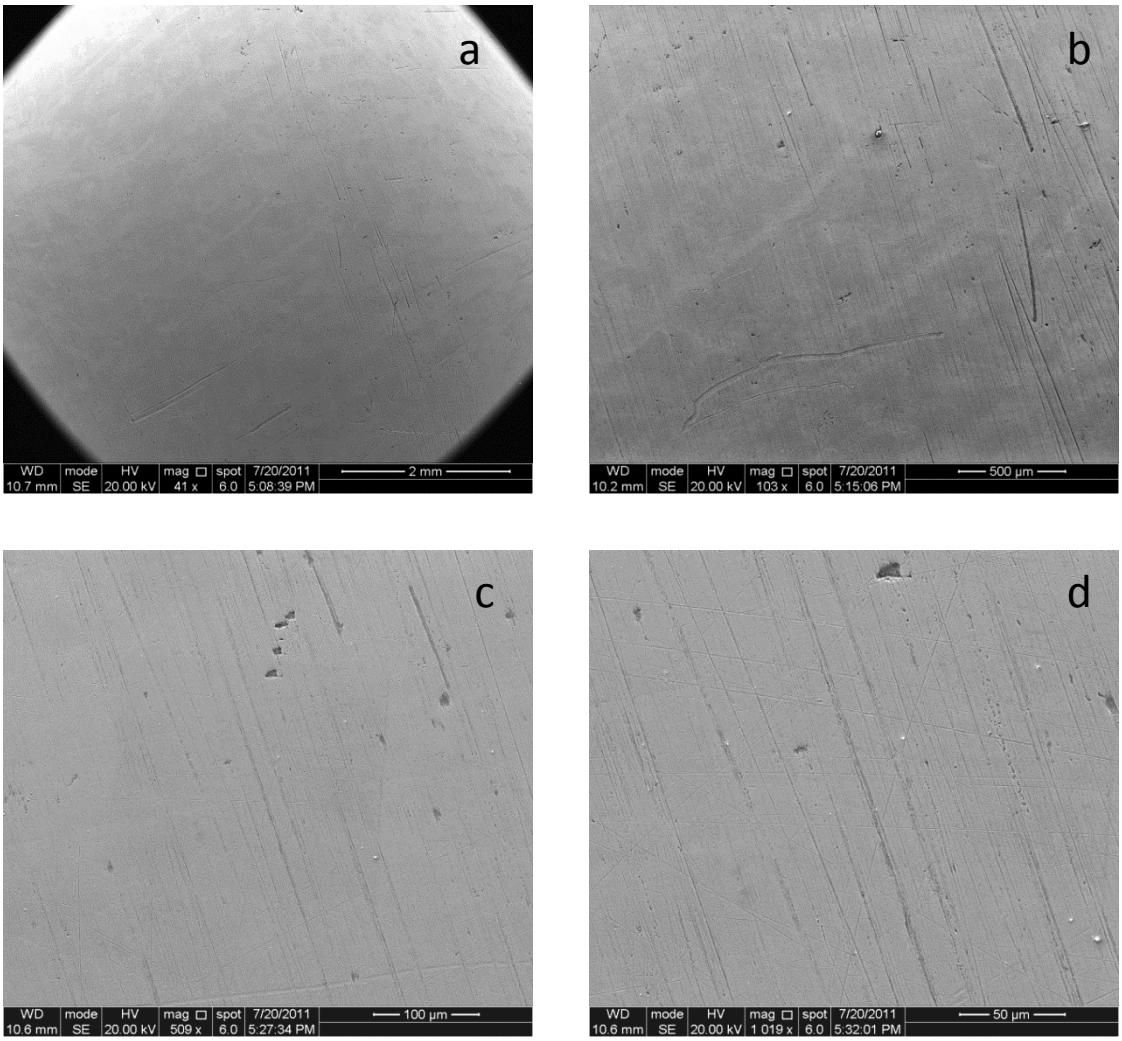


Figure 53: ESEM-EDX photomicrographs of sample Cu I six months after treatment with Liberon Brass and Copper Polish at magnifications of 40x (a), 100x (b), 500x (c) and 1000x (d).

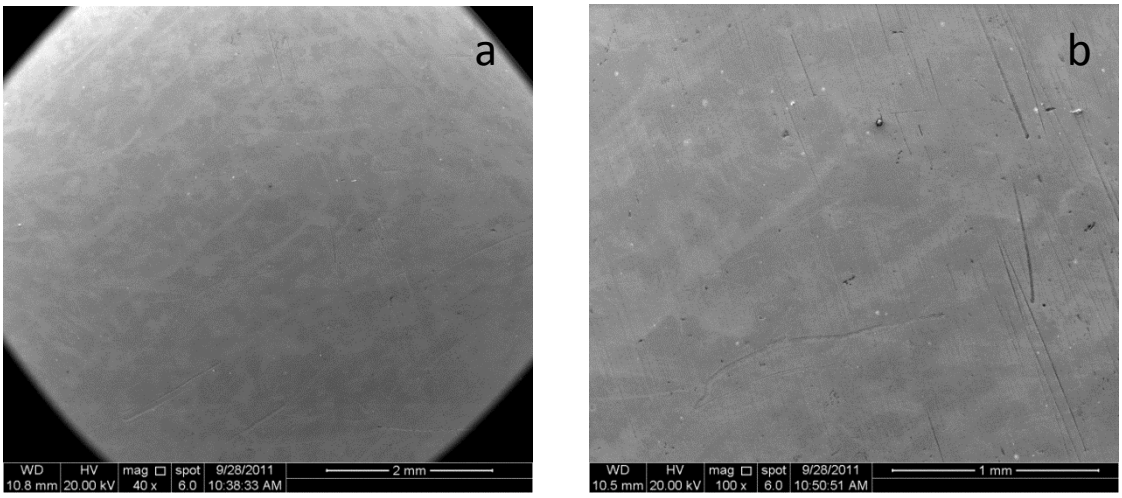
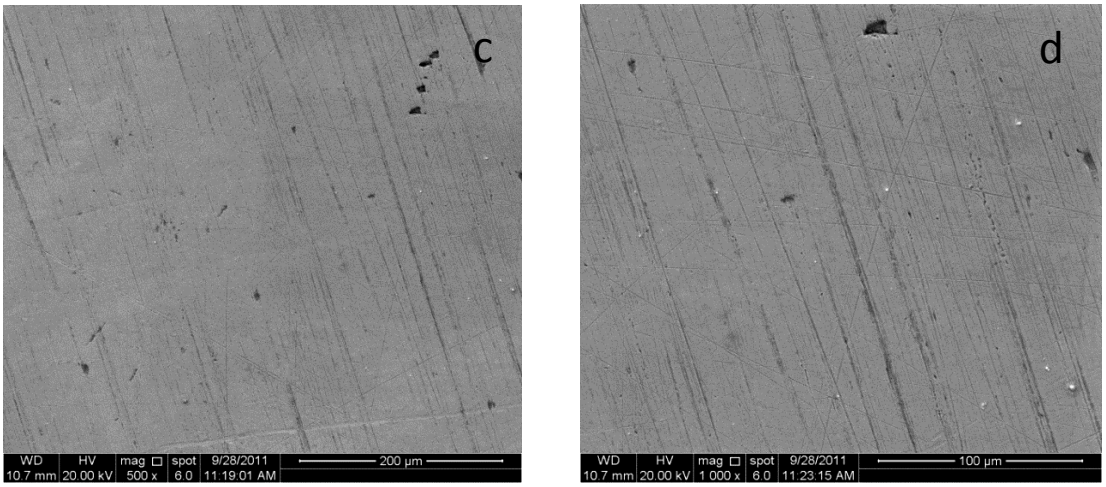


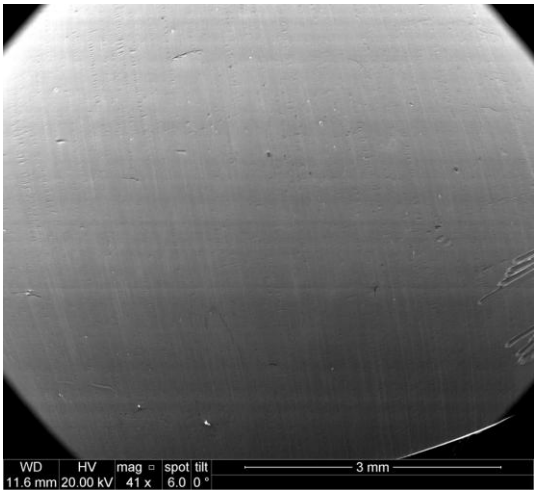
Figure 53 continued: ESEM-EDX photomicrographs of sample Cu I six months after treatment with Liberon Brass and Copper Polish at magnifications 40x (a), 100x (b), 500x (c) and 1000x (d).



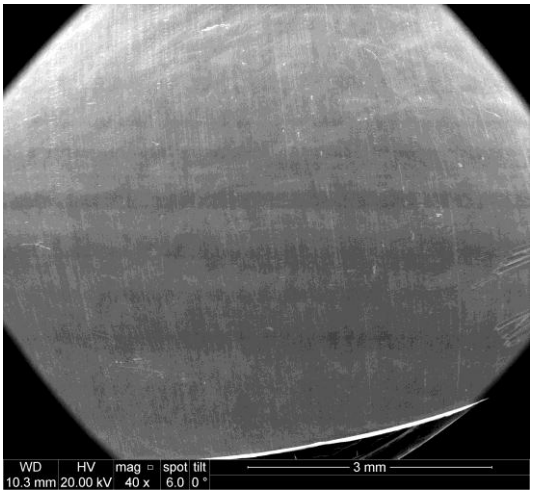
Cu II:

The ESEM photomicrographs of Cu II before and after treatment with Nevr Dull Wadding Polish at magnifications of c. 40x, 100x, 500x and 1000x are shown below. The surface of the Cu II coupon appeared to be uneven and scratched after treatment suggesting that the application of the Nevr Dull wadding had marked the copper surface. The scratches are clearer at magnifications of c. 100x and higher. The results are not surprising given that the Nevr Dull Wadding Polish contains lubricating oils which may not be easy to completely remove and traces may remain on the surface (Belman, 2004). Nevr Dull Wadding Polish also contains quartz and hematite as abrasives, which have a hardness of 7 and 6 on the Mohs hardness scale respectively, whereas copper has a hardness of 2.5-3 (Ted Pella Inc, 2013). The surface does however appear to be cleaner. The horizontal lines in the ESEM images are an artefact of the ESEM photomicrograph and not due to the treatment with Nevr Dull Wadding Polish.

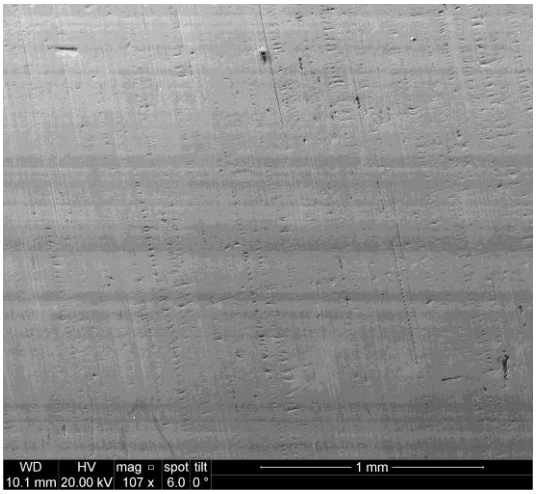
Figure 54: ESEM-EDX photomicrographs of sample Cu II before and after treatment with Nevr Dull Wadding Polish at magnifications of c. 40x, 100x, 500x and 1000x.



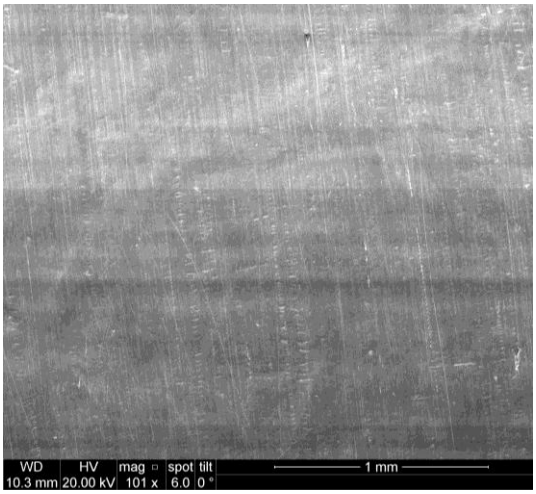
Before treatment at 41x



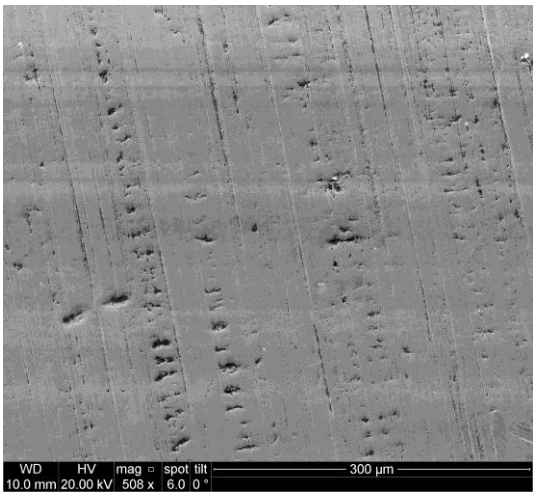
After treatment at 40x



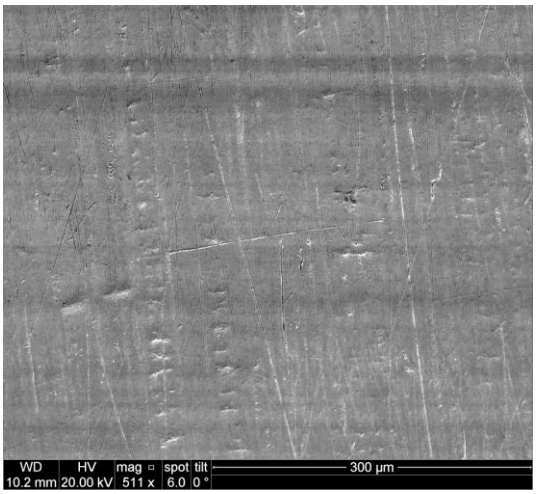
Before treatment at 107x



After treatment at 101x

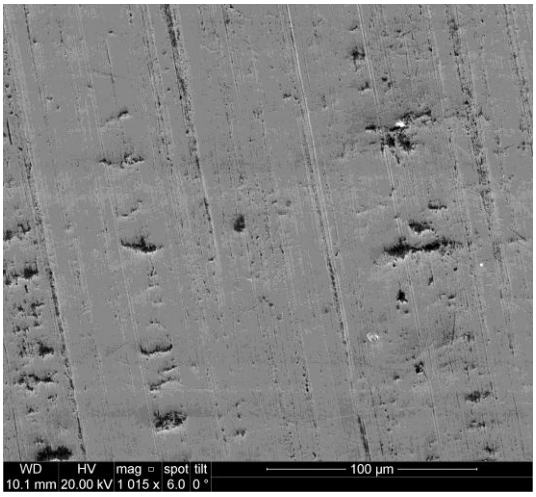


Before treatment at 508x

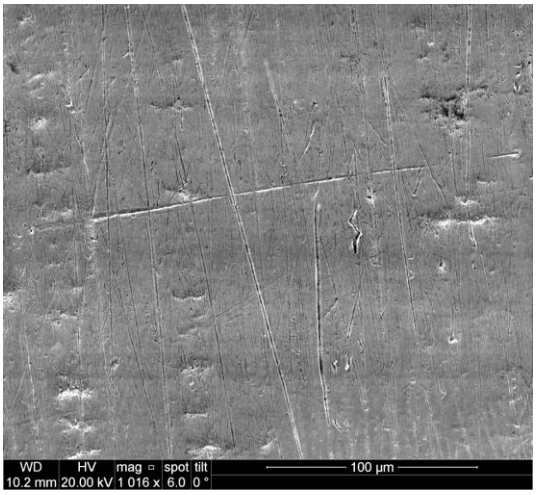


After treatment at 511x

Figure 54 continued: ESEM-EDX photomicrographs of sample Cu II before and after treatment with Nevr Dull Wadding Polish at magnifications of c. 40x, 100x, 500x and 1000x.



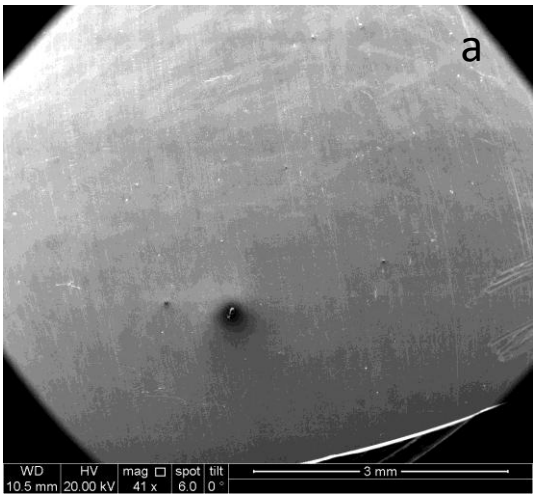
Before treatment at 1015x



After treatment at 1016x

The surface of the Cu II coupon appeared slightly less uneven over time at two, four and six months after treatment, which suggests a thin copper oxide layer may have formed. The scratches also appear to be slightly less distinct in the ESEM images over time after treatment. The ESEM photomicrographs of the Cu II coupon after two, four and six months at c. 40x, 100x, 500x and 1000x are as follows:

Figure 55: ESEM-EDX photomicrographs of sample Cu II two months after treatment with Nevr Dull Wadding Polish at magnifications of 41x (a), 101x (b), 512x (c) and 1015x (d).



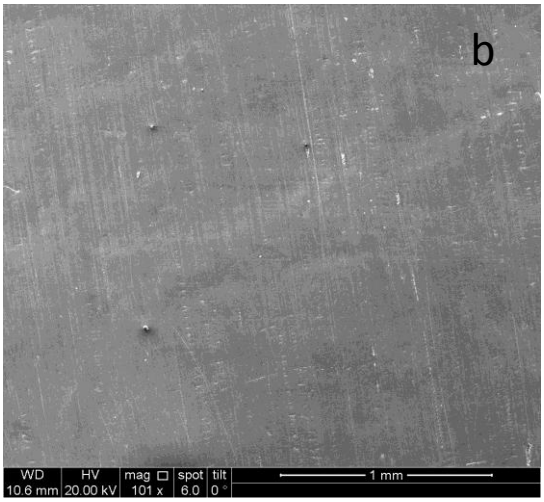


Figure 55 continued: ESEM-EDX photomicrographs of sample Cu II two months after treatment with Nevr Dull Wadding Polish at magnifications of 41x (a), 101x (b), 512x (c) and 1015x (d).

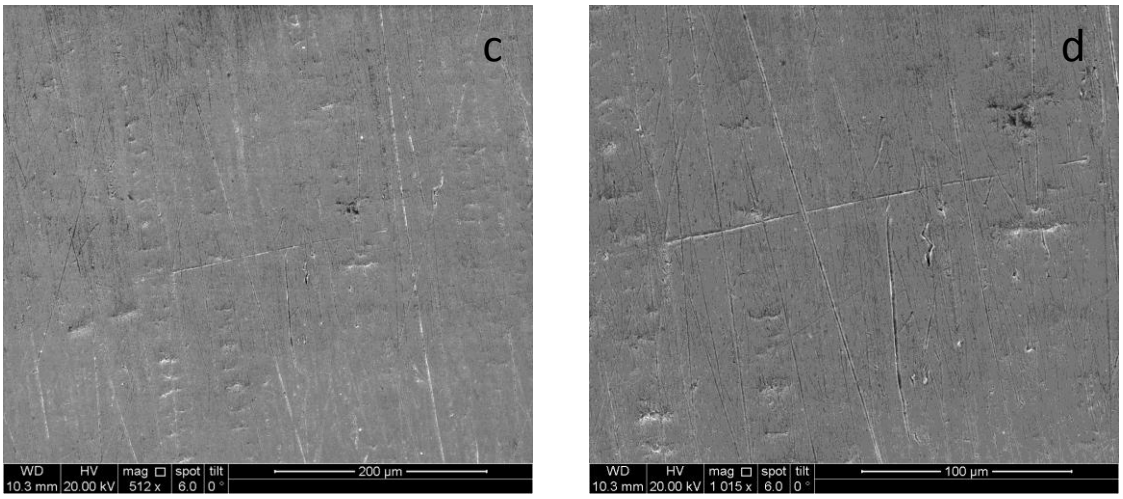


Figure 56: ESEM-EDX photomicrographs of sample Cu II four months after treatment with Nevr Dull Wadding Polish at magnifications of 40x (a), 101x (b), 508x (c) and 1002x (d).

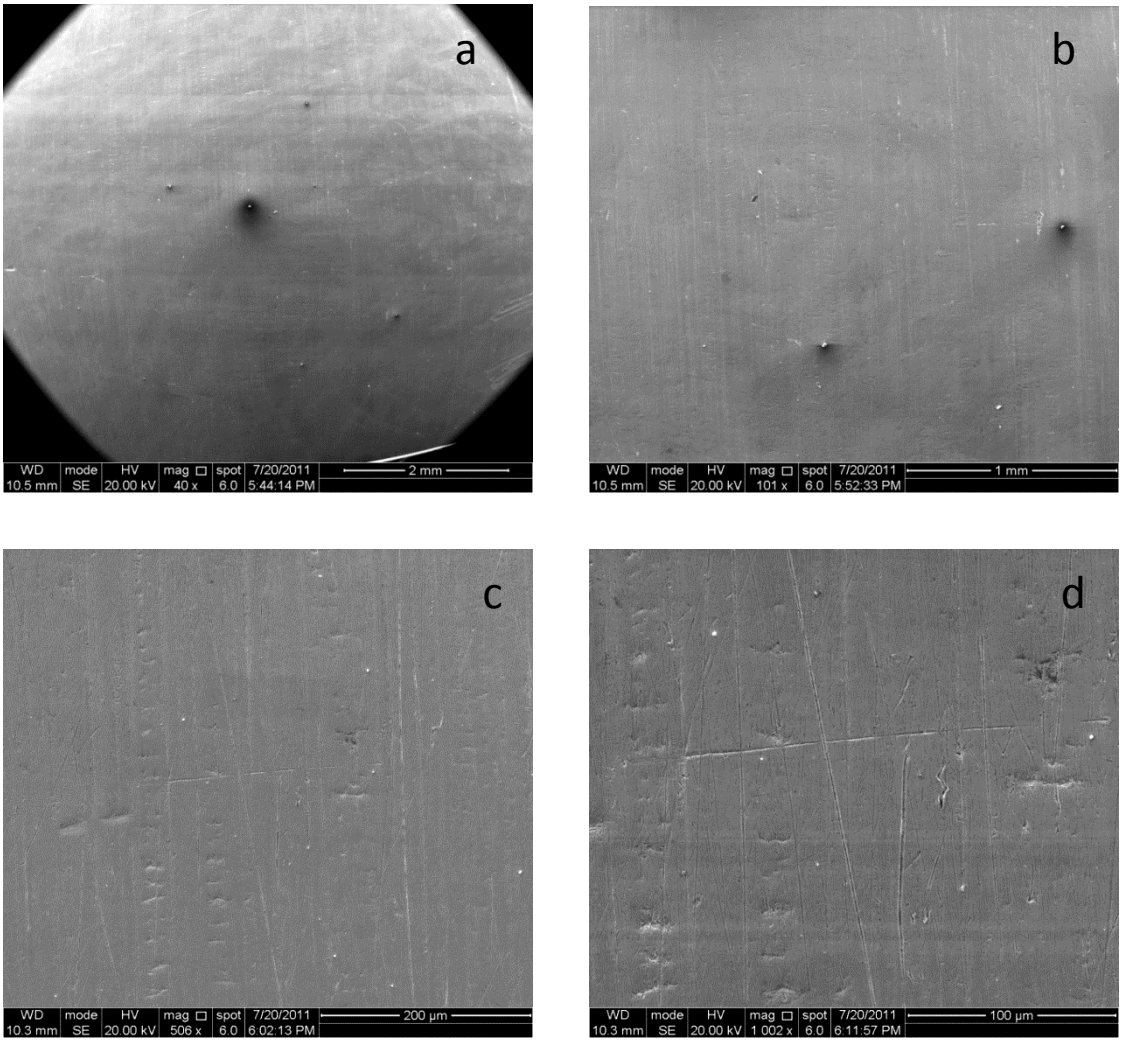
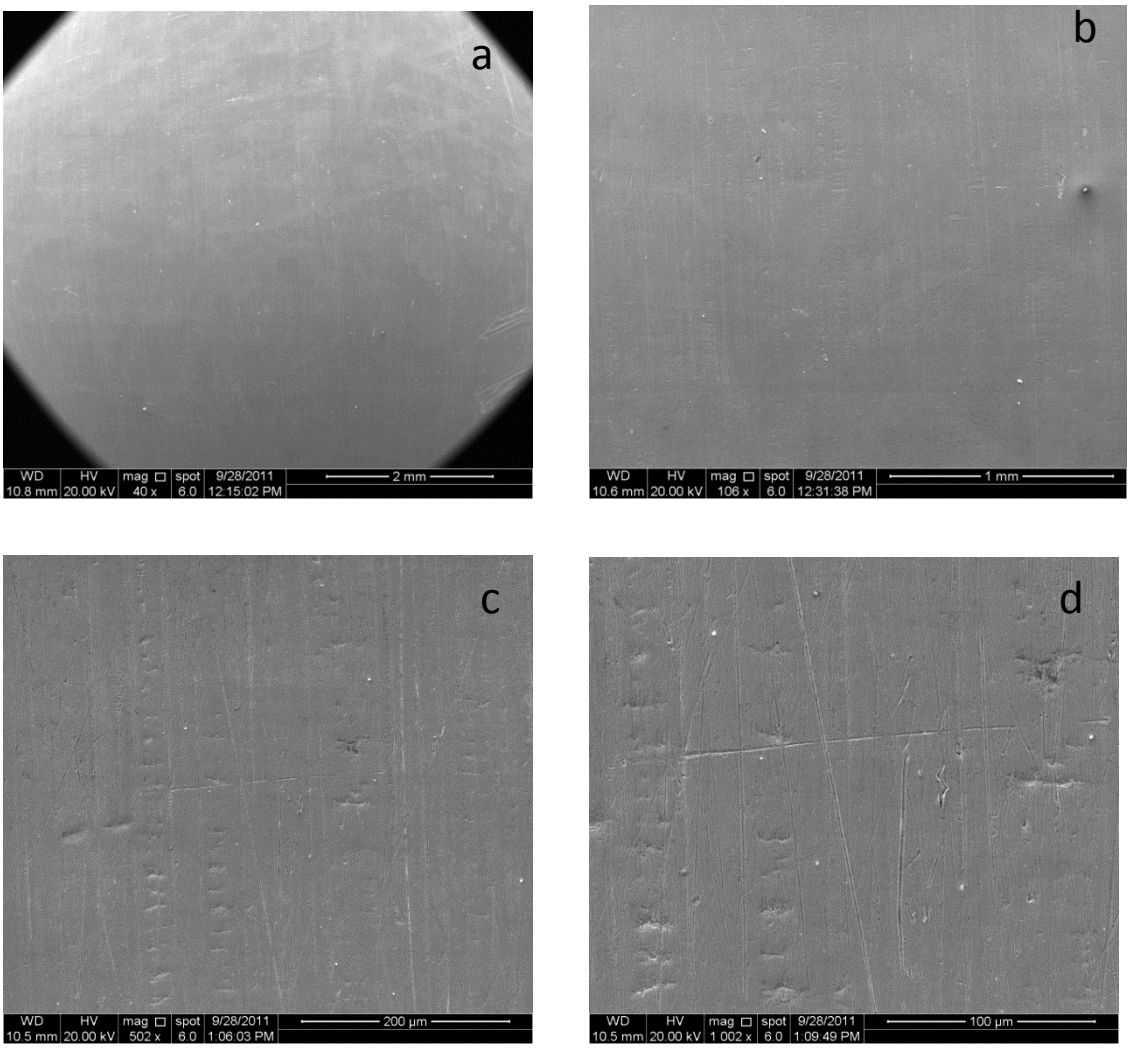


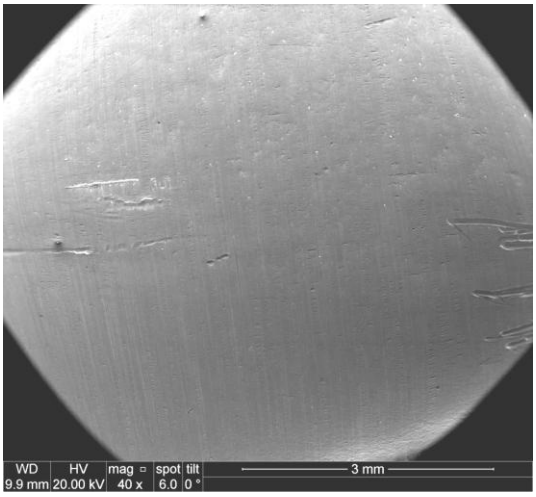
Figure 57: ESEM-EDX photomicrographs of sample Cu II six months after treatment with Nevr Dull Wadding Polish at magnifications of 40x (a), 106x (b), 502x (c) and 1002x (d).



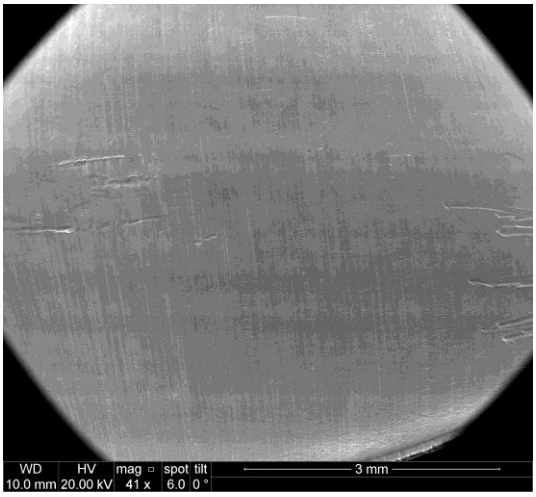
Cu III:

The ESEM photomicrographs of Cu III before and after treatment with Pre-Lim Surface Cleaner at magnifications of c. 40x, 100x, 500x and 1000x are shown below. The surface of the Cu III coupon appeared slightly uneven with fine vertical lines more visible after treatment. The surface also looks cleaner after treatment, particularly at higher magnifications such as c. 550x, with darker material in the scratches and indentations in the surface reduced. At the higher magnifications there also appear to be new scratches visible. Despite this, the Pre-Lim Surface Cleaner appears to be the mildest of the three treatments analysed for copper.

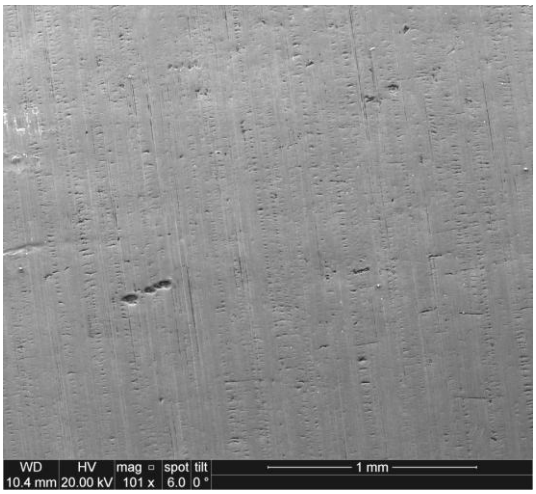
Figure 58: ESEM-EDX photomicrographs of sample Cu III before and after treatment with Pre-Lim Surface Cleaner at magnifications of c. 40x, 100x, 500x and 1000x.



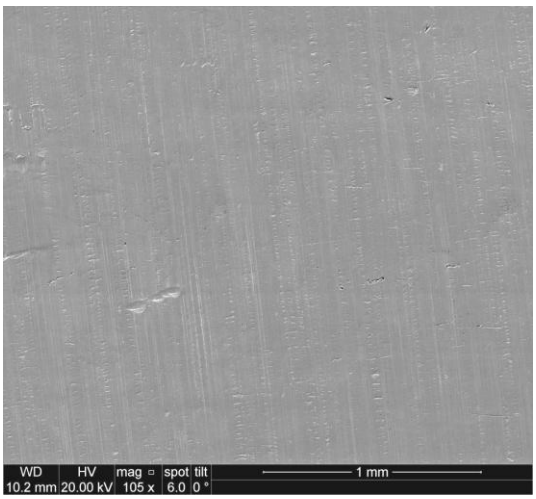
Before treatment at 40x



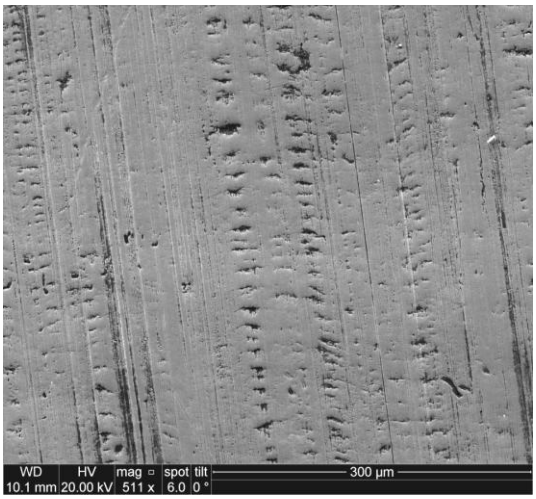
After treatment at 41x



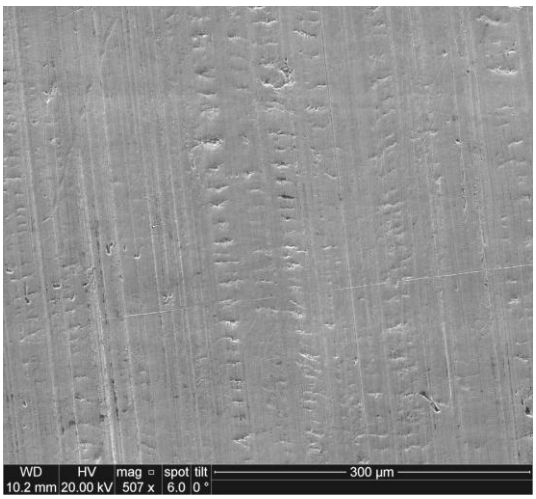
Before treatment at 101x



After treatment at 105x

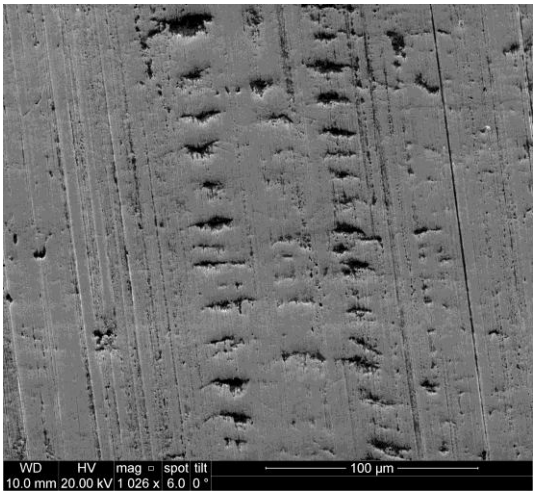


Before treatment at 511x

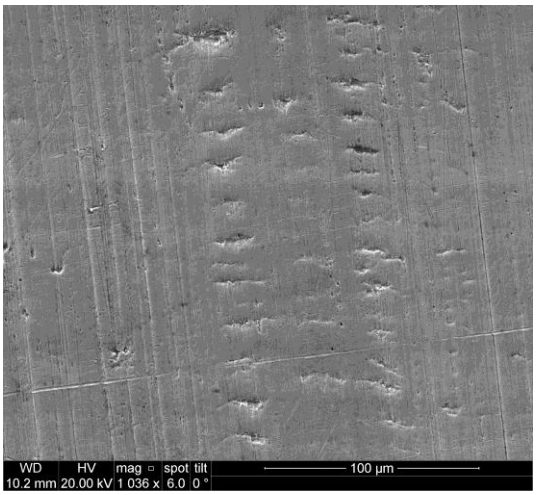


After treatment at 507x

Figure 58 continued: ESEM-EDX photomicrographs of sample Cu III before and after treatment with Pre-Lim Surface Cleaner at magnifications of c. 40x, 100x, 500x and 1000x.



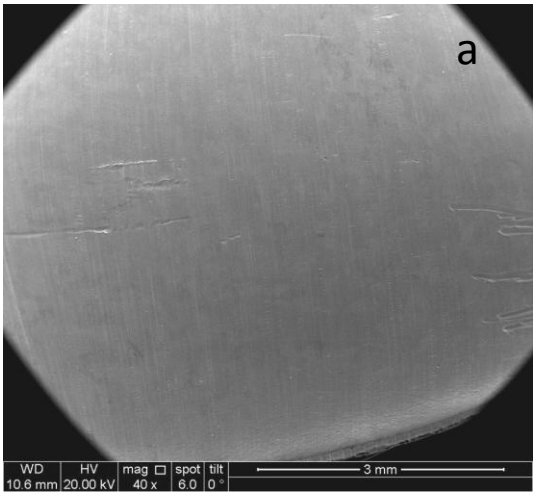
Before treatment at 1026x



After treatment at 1036x

The surface of the Cu III coupon appeared to be more even over time at two, four and six months after treatment, which suggests that a thin copper oxide layer may have formed. The ESEM photomicrographs of the Cu III coupon after two, four and six months at c. 40x, 100x, 500x and 1000x are as follows:

Figure 59: ESEM-EDX photomicrographs of sample Cu III two months after treatment with Pre-Lim Surface Cleaner at magnifications of 40x (a), 108x (b), 503x (c) and 1042x (d).



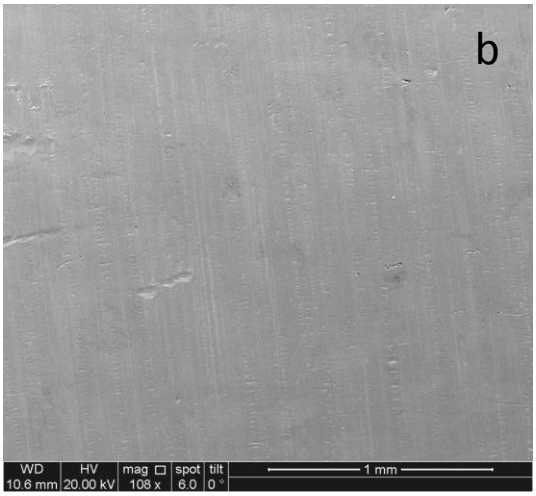


Figure 59 continued: ESEM-EDX photomicrographs of sample Cu III two months after treatment with Pre-Lim Surface Cleaner at magnifications of 40x (a), 108x (b), 503x (c) and 1042x (d).

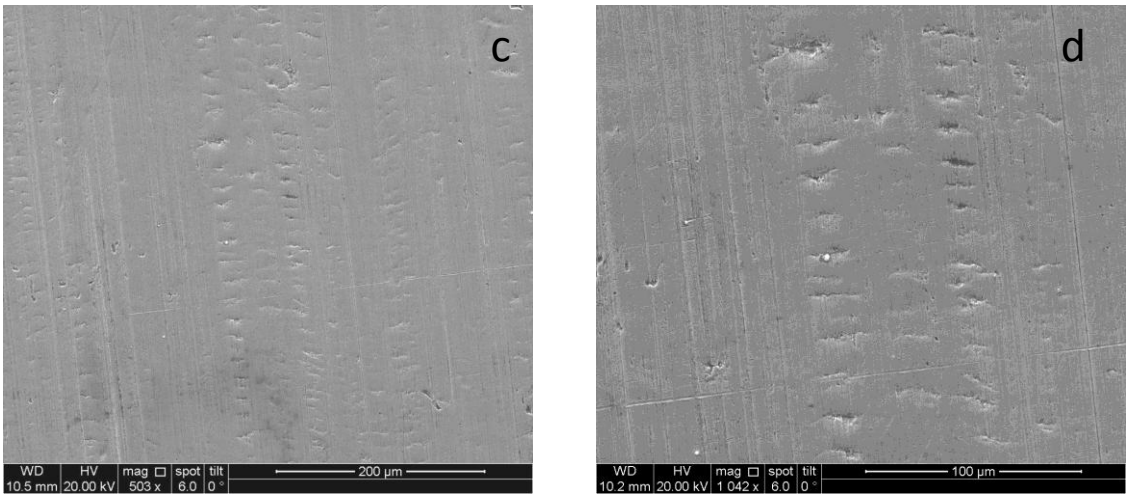


Figure 60: ESEM-EDX photomicrographs of sample Cu III four months after treatment with Pre-Lim Surface Cleaner at magnifications of 41x (a), 105x (b), 509x (c) and 1015x (d).

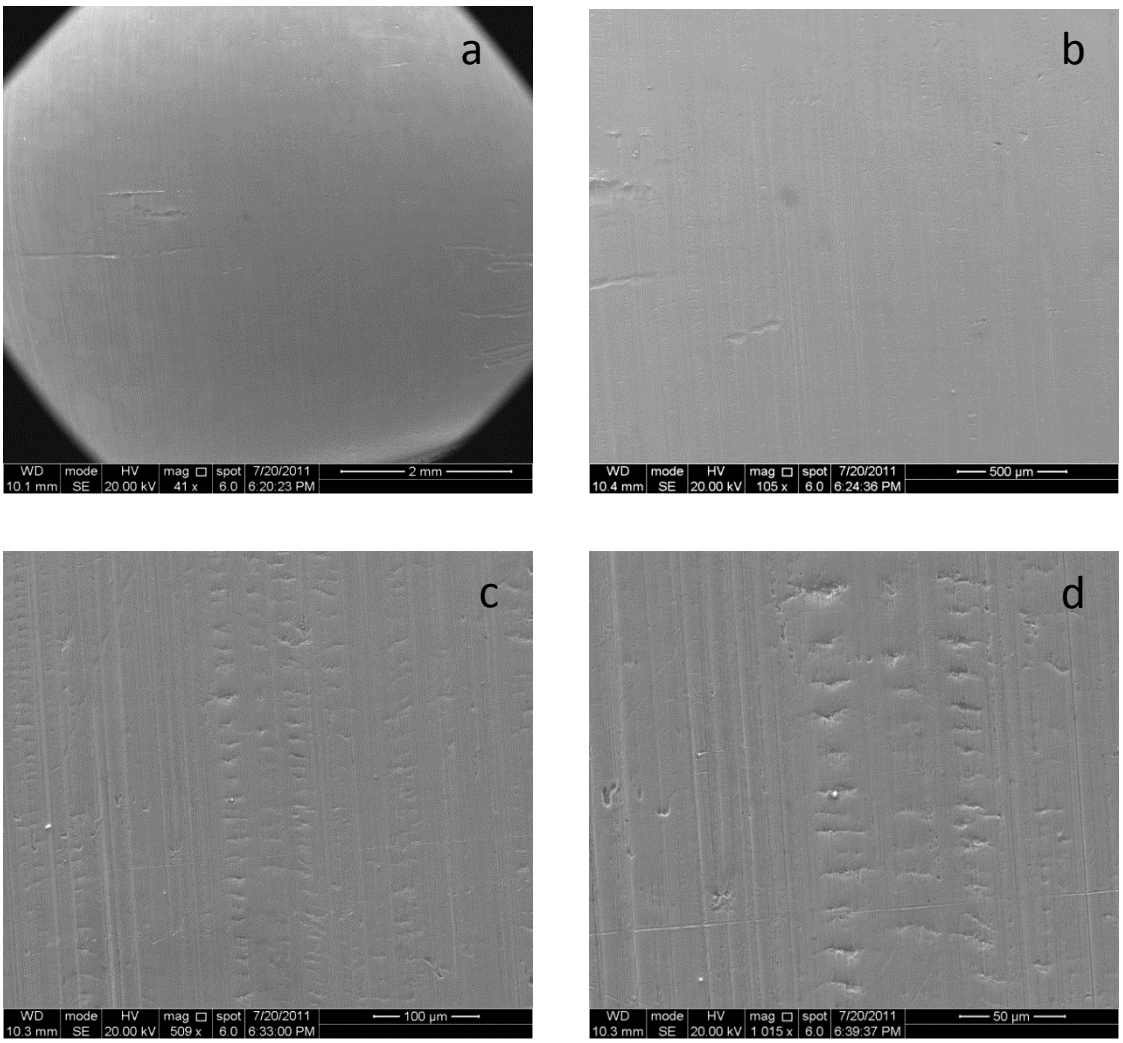
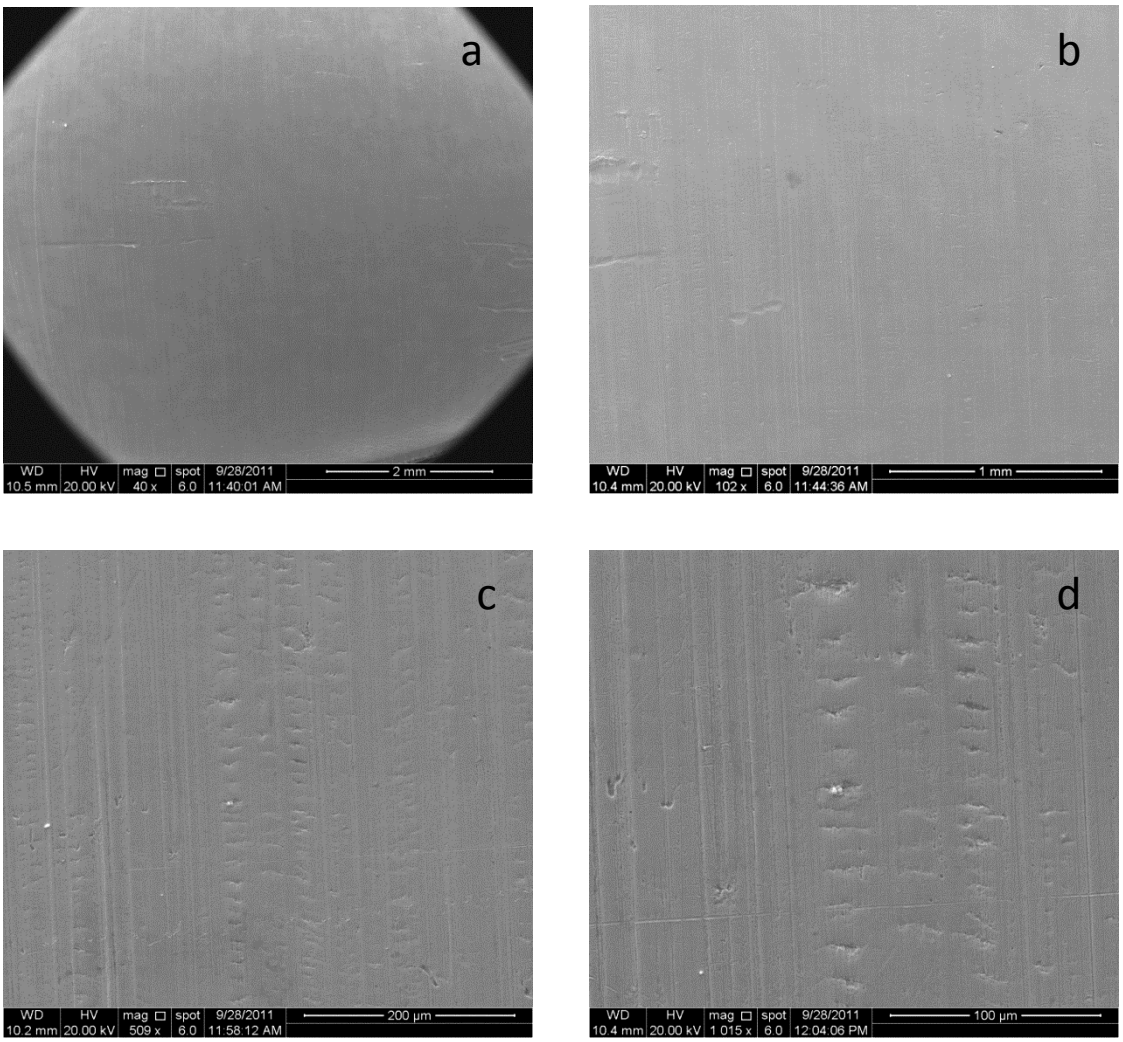


Figure 61: ESEM-EDX photomicrographs of sample Cu III six months after treatment with Pre-Lim Surface Cleaner at magnifications of 40x (a), 102x (b), 509x (c) and 1015x (d).



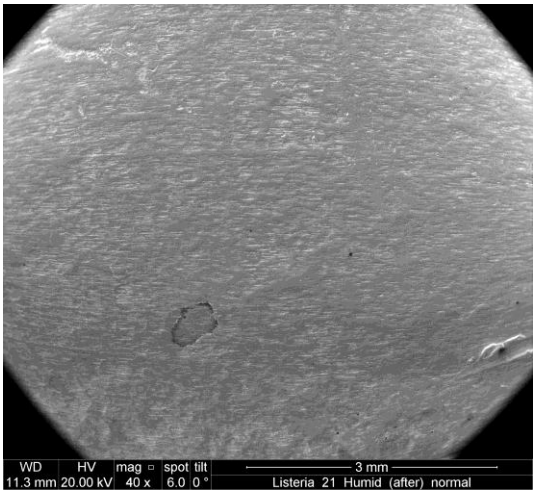
4.6.3 Lead Coupons

Pb I:

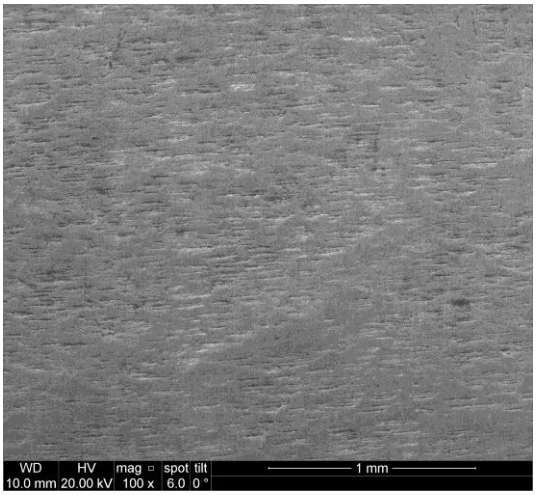
The ESEM photomicrographs of Pb I before and after treatment with 5 % w/v disodium EDTA in deionised water at magnifications of c. 40x, 100x, 500x and 1000x are shown below. The surface of the Pb I coupon appeared to be patchy after treatment and there was a dark rimmed deposit visible from 40x magnification, which could be a residue from the disodium EDTA solution. With higher magnifications the lead surface appears cleaner. There also appear to be minor scratches visible in the surface after treatment at higher magnifications of c. 1000x, which may be due to abrasion from the cotton swabs used to apply the disodium EDTA solution on the relatively soft lead metal.

Figure 62: ESEM-EDX photomicrographs of sample Pb I before and after treatment with 5 % w/v disodium EDTA in deionised water at magnifications of c. 40x, 100x, 500x and 1000x.

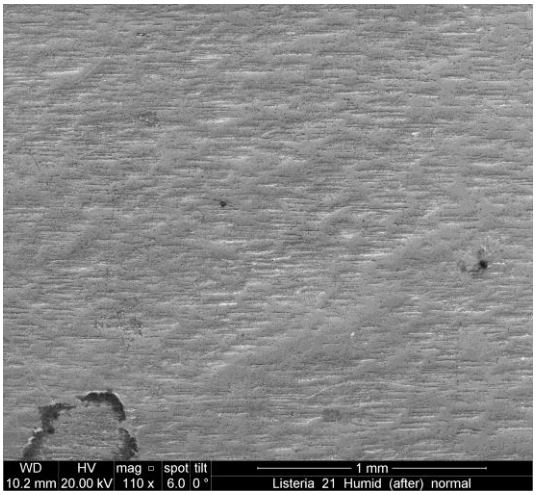
Before treatment at 41x



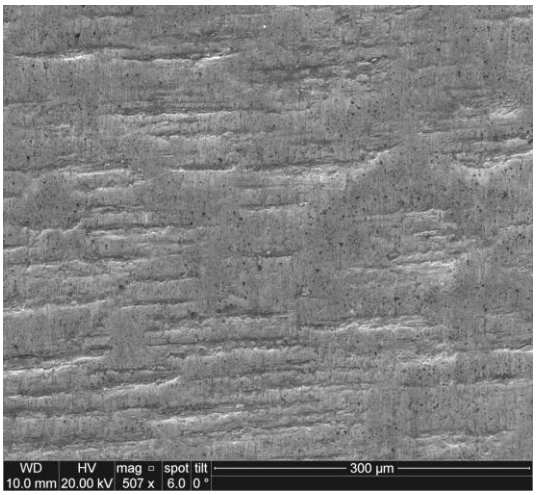
After treatment at 40x



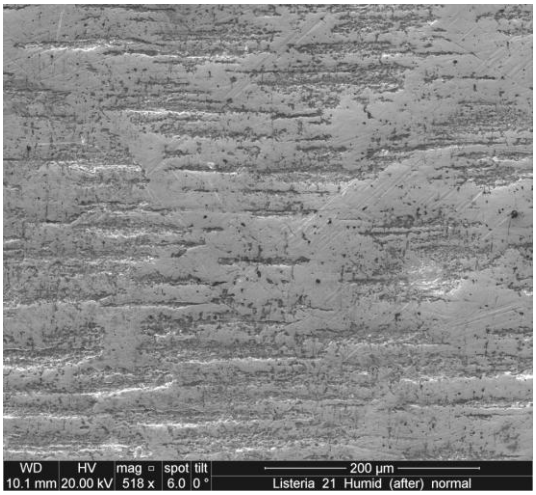
Before treatment at 100x



After treatment at 110x

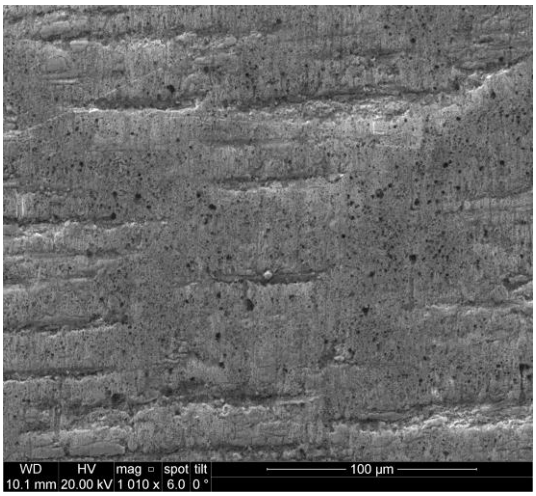


Before treatment at 507x

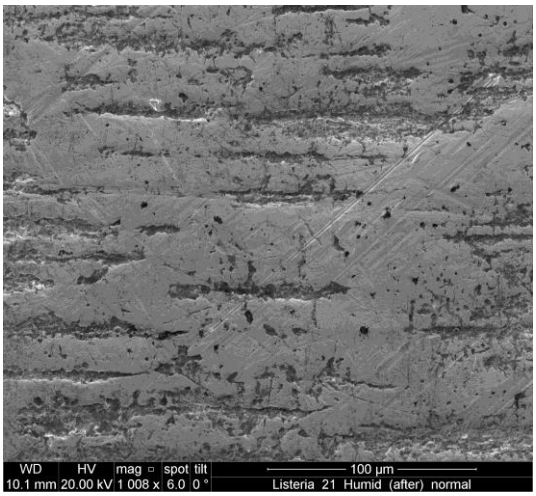


After treatment at 518x

Figure 62 continued: ESEM-EDX photomicrographs of sample Pb I before and after treatment with 5 % w/v disodium EDTA in deionised water at magnifications of c. 40x, 100x, 500x and 1000x.



Before treatment at 1010x



After treatment at 1008x

EDX analysis at a magnification of 2018x was carried out on part of the dark rimmed deposit on the Pb I coupon after treatment with 5 % w/v disodium EDTA in deionised water and the results are shown in **Figure 63**. Sodium, calcium and potassium were identified, as well as lead, oxygen, carbon and silicon which were identified in the lead control coupon IV at a magnification of c. 100x. The sodium could be due to residues from the disodium EDTA, and further analysis is required to investigate the presence of the calcium and potassium.

Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	O	Na	Si	K	Ca	Pb	Total
Spectrum 1	Yes	8.85	24.87	1.68	0.79	0.62	1.50	61.68	100.00
Mean		8.85	24.87	1.68	0.79	0.62	1.50	61.68	100.00
Std. deviation		0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Max.		8.85	24.87	1.68	0.79	0.62	1.50	61.68	
Min.		8.85	24.87	1.68	0.79	0.62	1.50	61.68	

All results in weight%

INCA

Figure 63: EDX results for the dark edged deposit on Pb I after treatment with 5 % w/v disodium EDTA in deionised water.

The surface of the Pb I coupon appeared to be more even over time at two, four and six months after treatment, which suggests that a thin lead oxide layer may have formed on the surface. The dark rimmed deposit was still visible from magnifications of 40x and the scratches at the higher magnifications of c. 500x and 100x were also still visible. The ESEM photomicrographs of the Pb I coupon after two, four and six months at magnifications of c. 40x, 100x, 500x and 1000c are as follows:

Figure 64: ESEM-EDX photomicrographs of sample Pb I two months after treatment with 5 % w/v disodium EDTA in deionised water at magnifications of 40x (a), 102x (b), 505x (c) and 1010x (d).

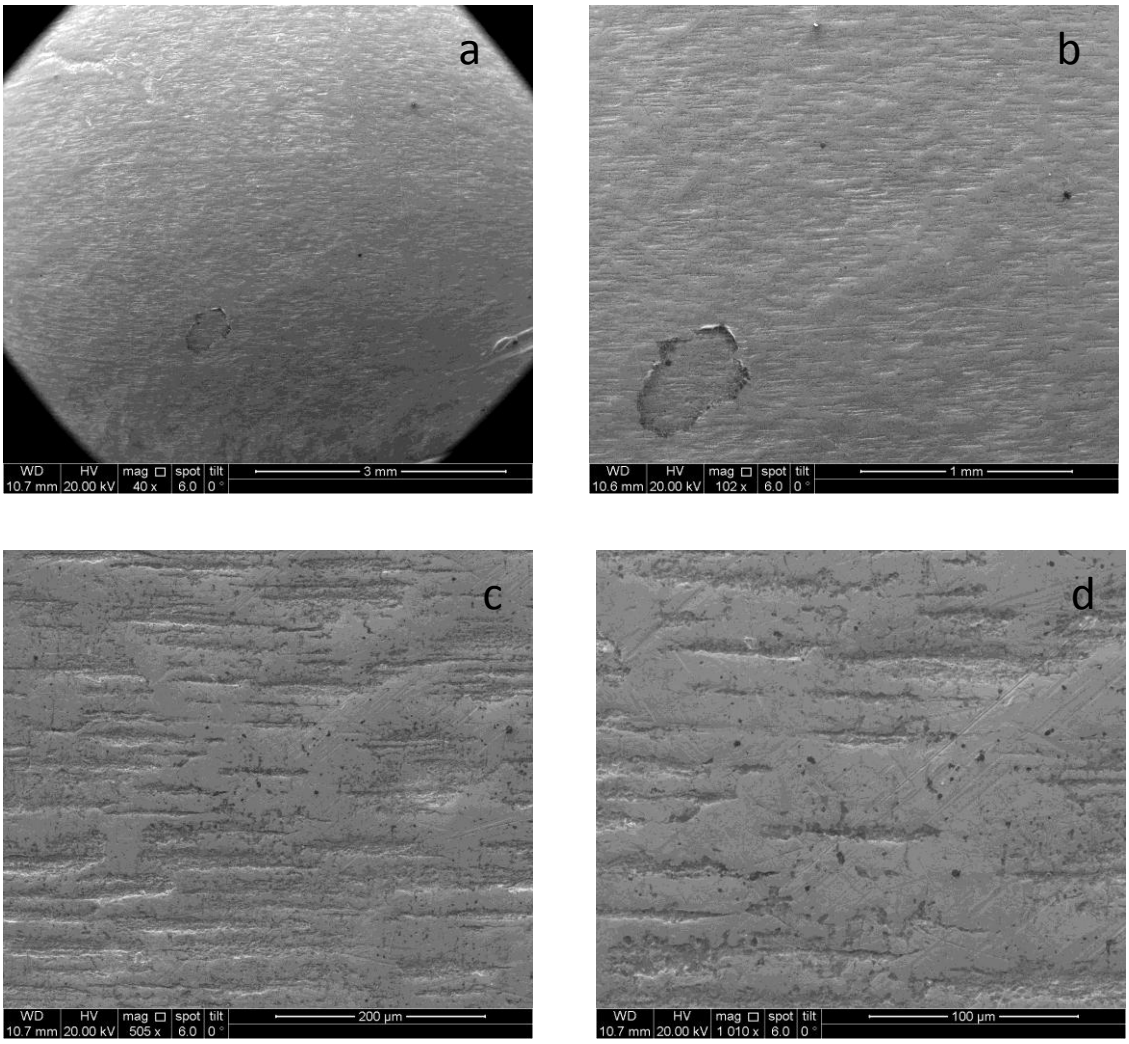


Figure 65: ESEM-EDX photomicrographs of sample Pb I four months after treatment with 5 % w/v disodium EDTA in deionised water at magnifications of 40x (a), 102x (b), 509x (c) and 1020x (d).

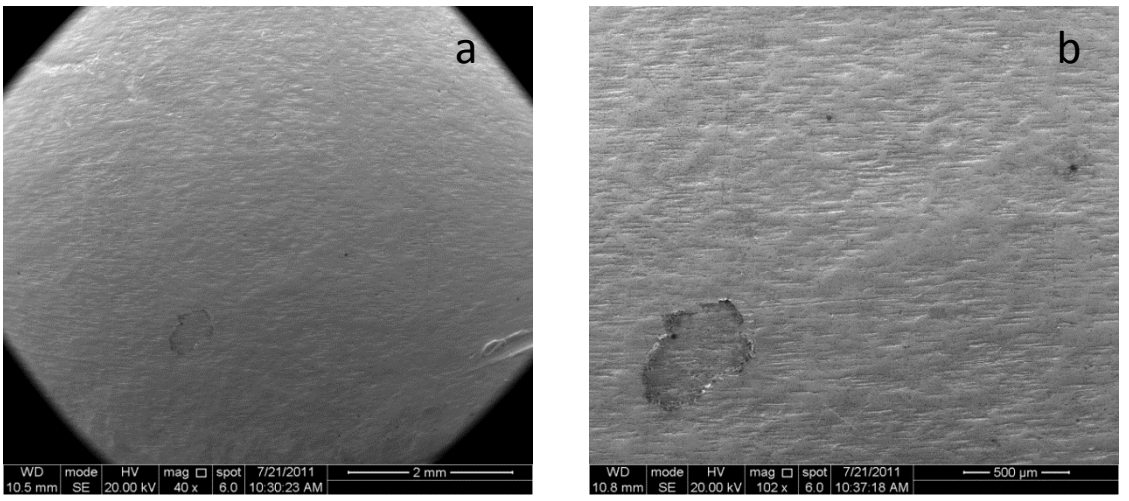
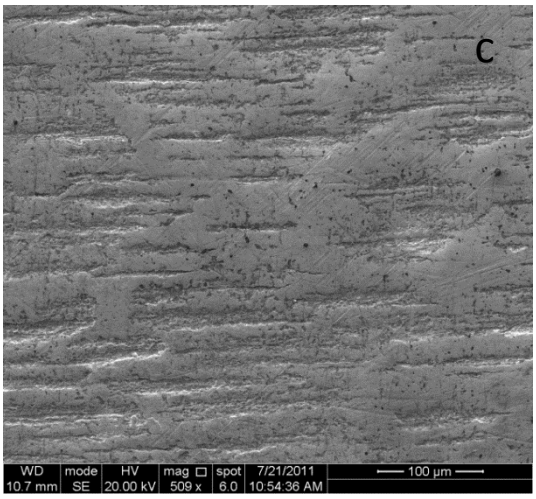


Figure 65 continued: ESEM-EDX photomicrographs of sample Pb I four months after treatment with 5 % w/v disodium EDTA in deionised water at magnifications of 40x (a), 102x (b), 509x (c) and 1020x (d).



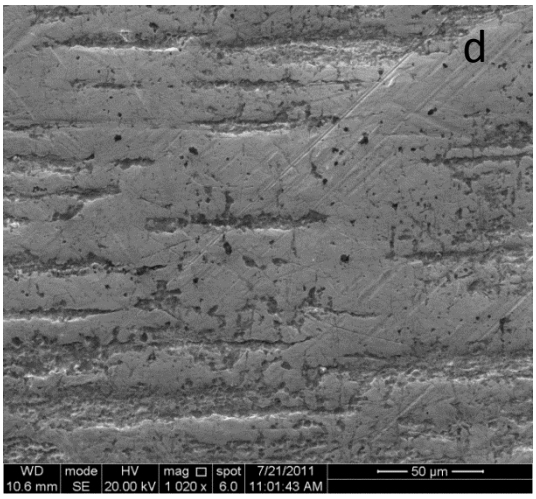
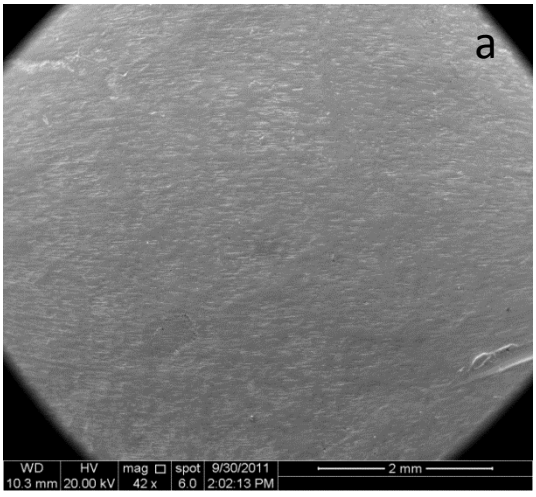
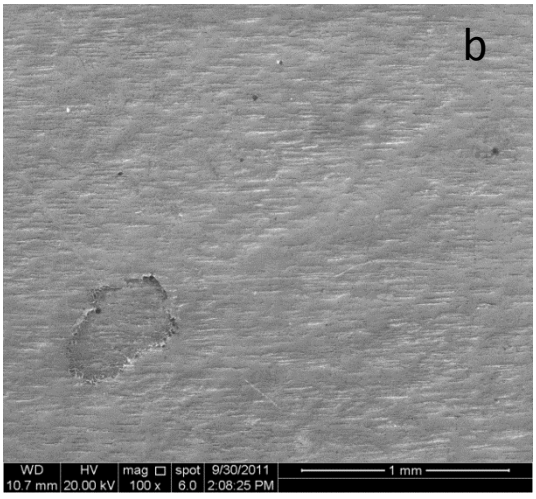
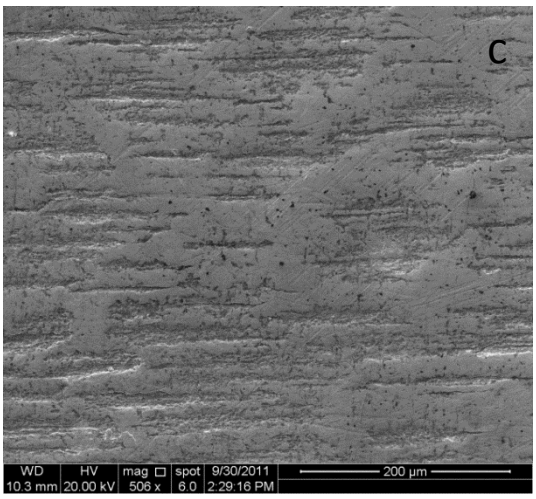
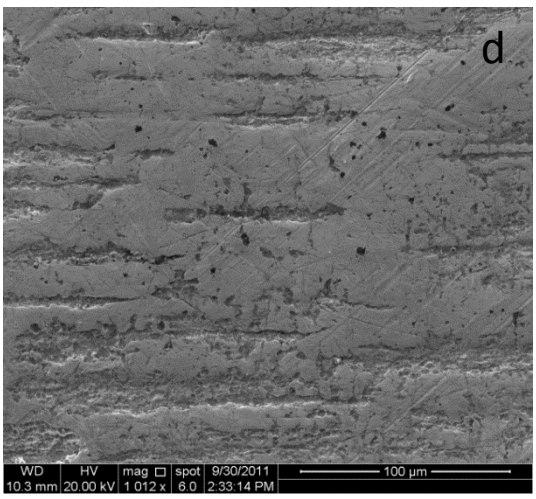


Figure 66: ESEM-EDX photomicrographs of sample Pb I six months after treatment with 5 % w/v disodium EDTA in deionised water at magnifications of 42x (a), 100x (b), 506x (c) and 1012x (d).





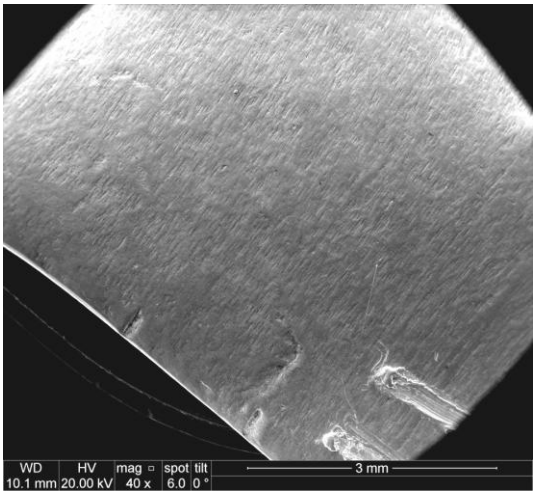




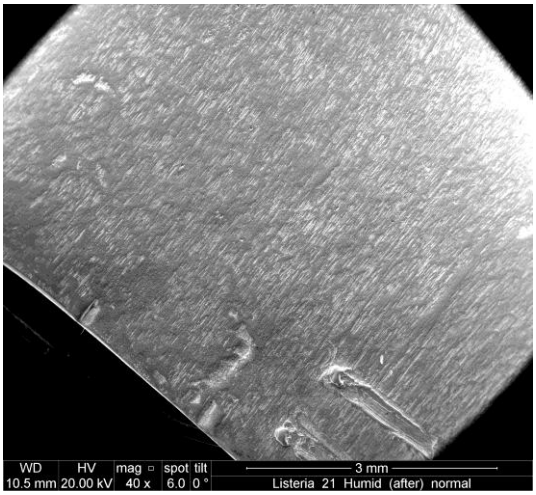
Pb II:

The ESEM photomicrographs for Pb II before and after treatment with 5 % w/v disodium EDTA in boiled deionised water at magnifications of c. 40x, 100x, 500x and 1000x are shown below. The Pb II coupon also appeared to be slightly patchy after treatment at 40x magnification, but at higher magnifications of c. 100x, 500x and 1000x the lead surface appeared cleaner and relatively even. The 5 % w/v disodium EDTA solution prepared with boiled deionised water appeared to be milder than the disodium EDTA solution prepared with deionised water used on Pb I. This is consistent with the conservation literature, as boiled deionised water is recommended for use in the conservation of lead objects (Selwyn, 2004: 119). At higher magnifications such as c. 1000x minor scratches were visible, which may be due to abrasion from the cotton swab used to apply the disodium EDTA solution, as mentioned with the Pb I coupon.

Figure 67: ESEM-EDX photomicrographs of sample Pb II before and after treatment with 5 % w/v disodium EDTA in boiled deionised water at magnifications of c. 40x, 100x, 500x and 1000x.

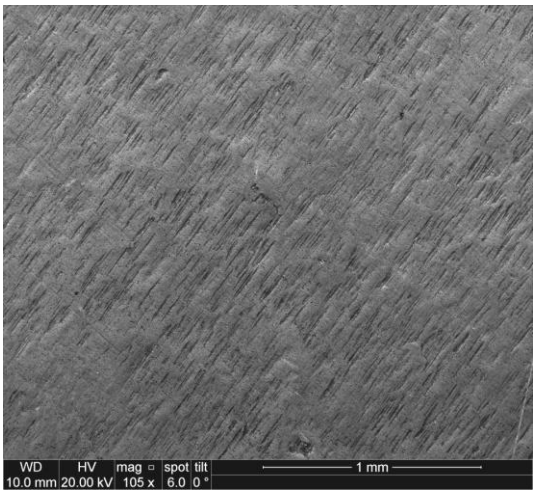


Before treatment at 40x

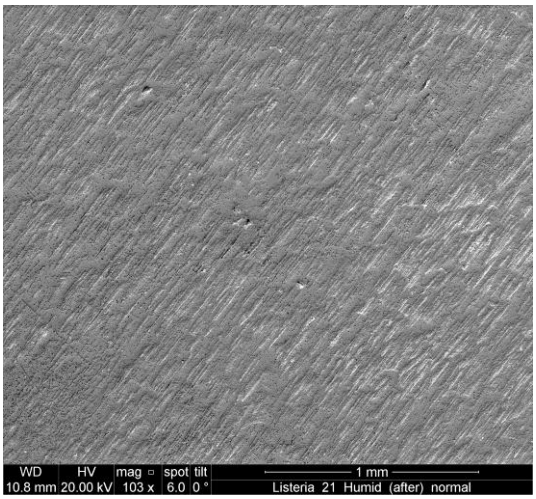


After treatment at 40x

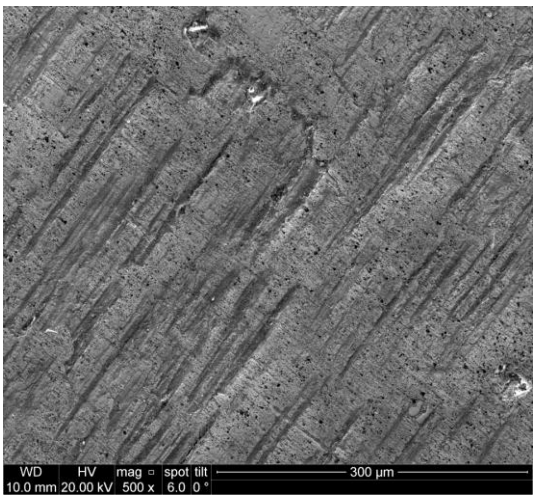
Figure 67 continued: ESEM-EDX photomicrographs of sample Pb II before and after treatment with 5 % w/v disodium EDTA in boiled deionised water at magnifications of c. 40x, 100x, 500x and 1000x.



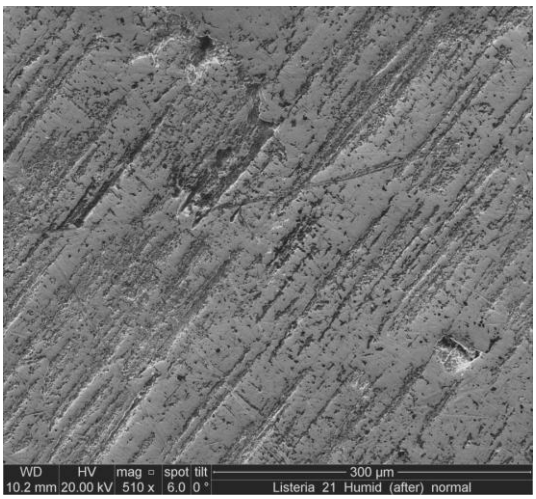
Before treatment at 105x



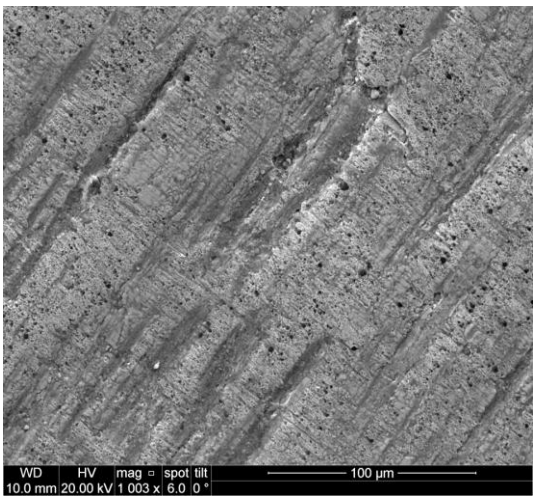
After treatment at 103x



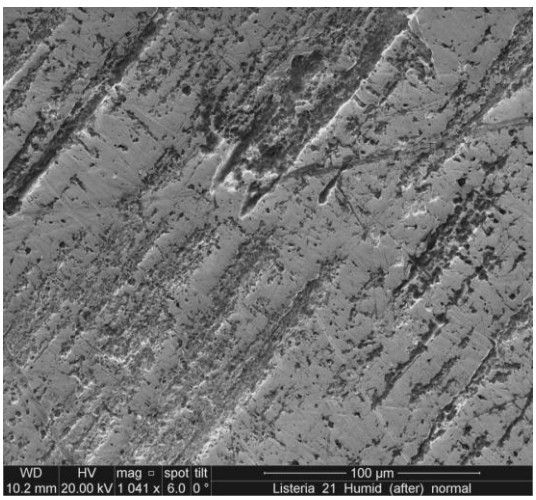
Before treatment at 500x



After treatment at 510x



Before treatment at 1003x



After treatment at 1041x

The surface of the Pb II coupon appeared to be more even over time at two, four and six months after treatment, which suggests that a thin lead oxide layer may have formed on the surface, as in the Pb I coupon. The ESEM photomicrographs of the Pb II coupon after two, four and six months at c. 40x, 100x, 500x and 1000x are as follows:

Figure 68: ESEM-EDX photomicrographs of sample Pb II two months after treatment with 5 % w/v disodium EDTA in boiled deionised water at magnifications of 41x (a), 104x (b), 510x (c) and 1014x (d).

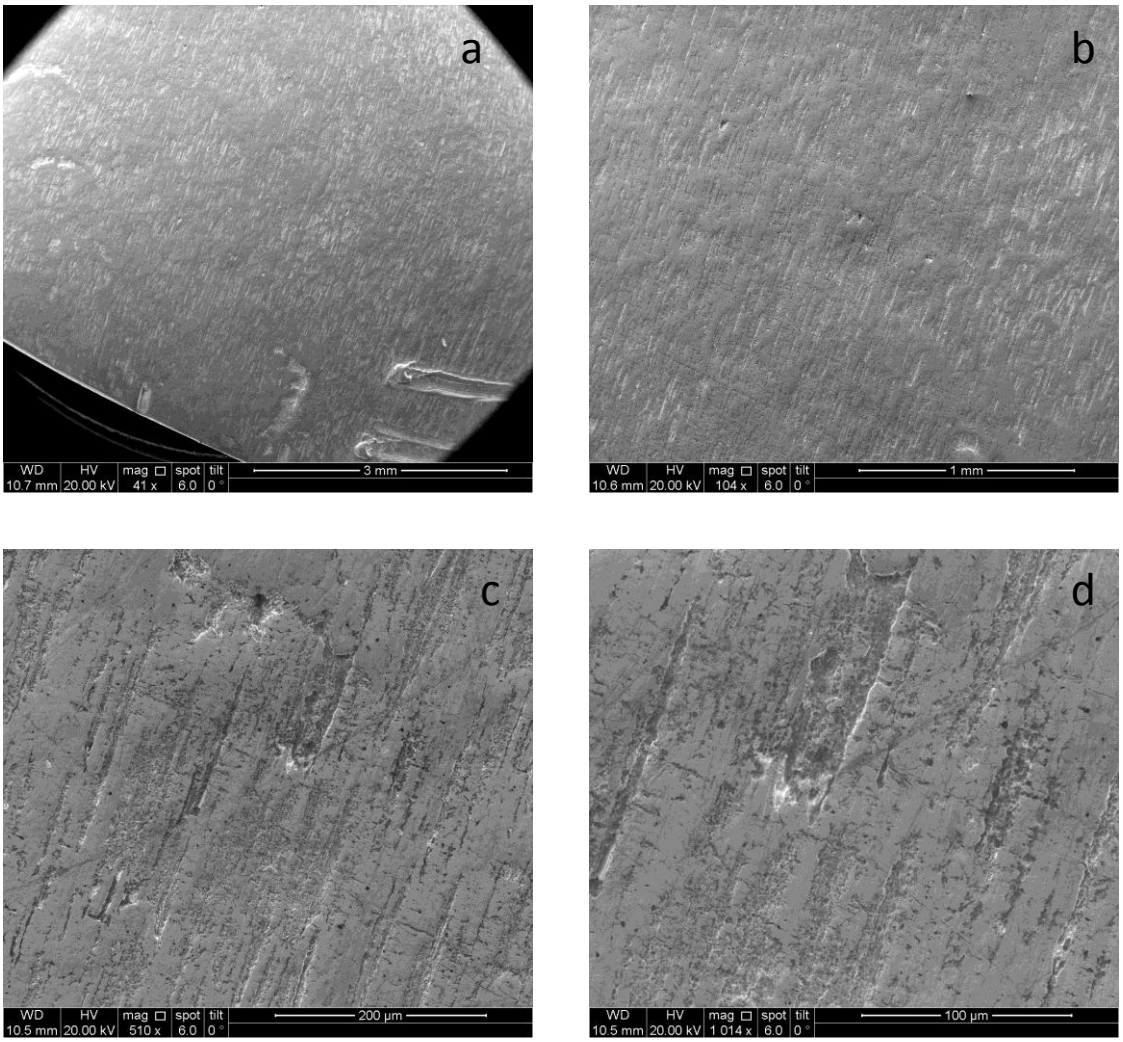


Figure 69: ESEM-EDX photomicrographs of sample Pb II four months after treatment with 5 % w/v disodium EDTA in boiled deionised water at magnifications of 40x (a), 103x (b), 505x (c) and 1012x (d).

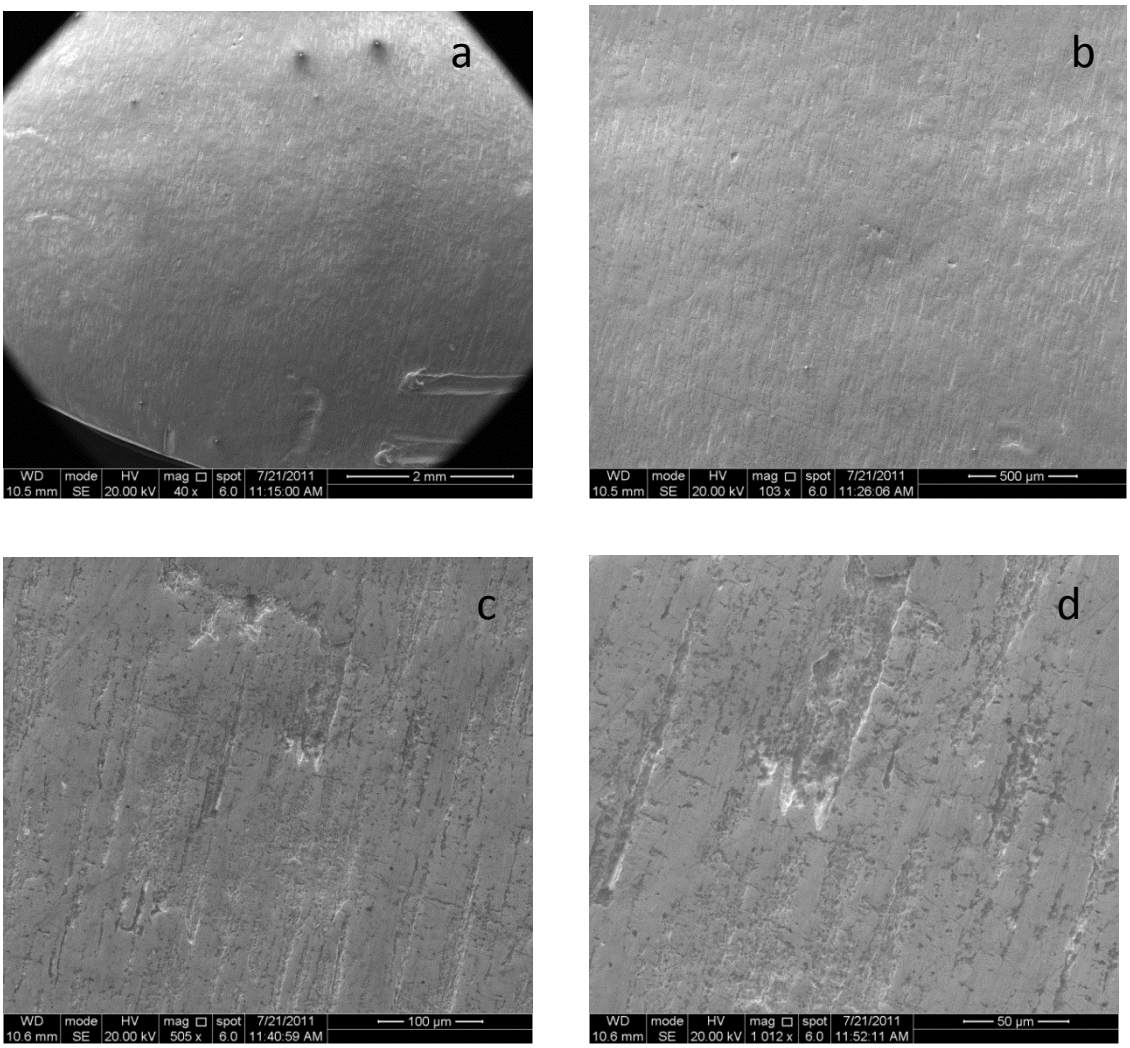


Figure 70: ESEM-EDX photomicrographs of sample Pb II six months after treatment with 5 % w/v disodium EDTA in boiled deionised water at magnifications of 40x (a), 100x (b), 500x (c) and 1000x (d).

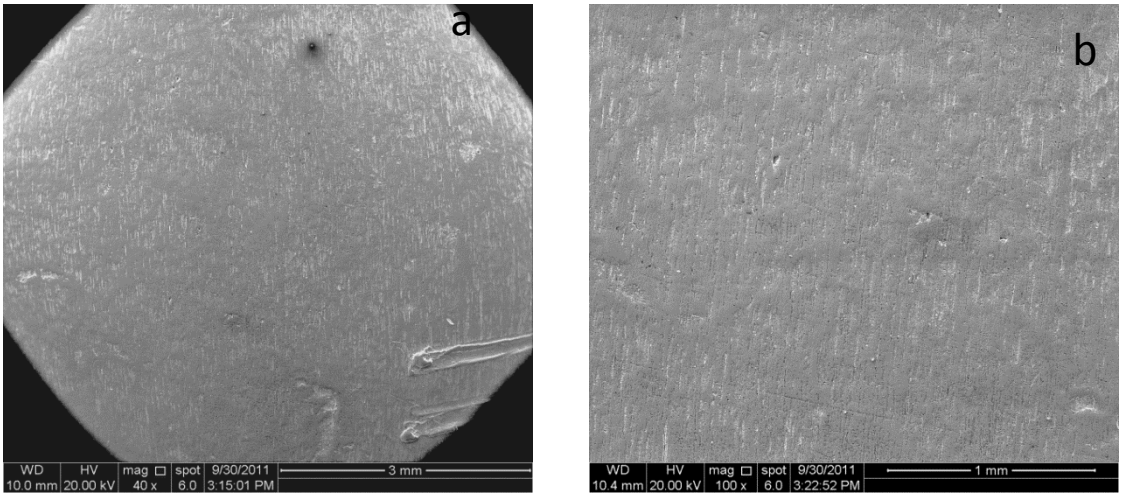
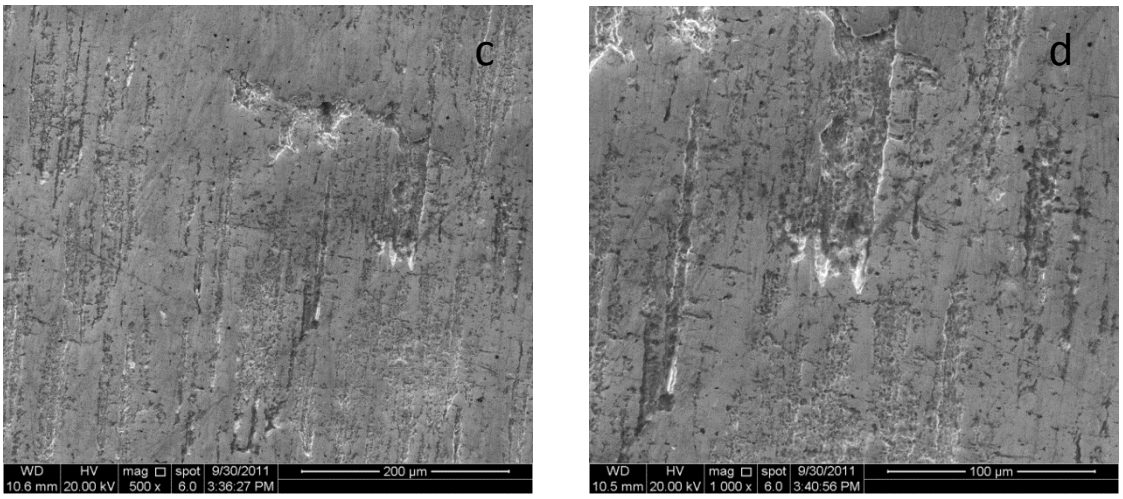


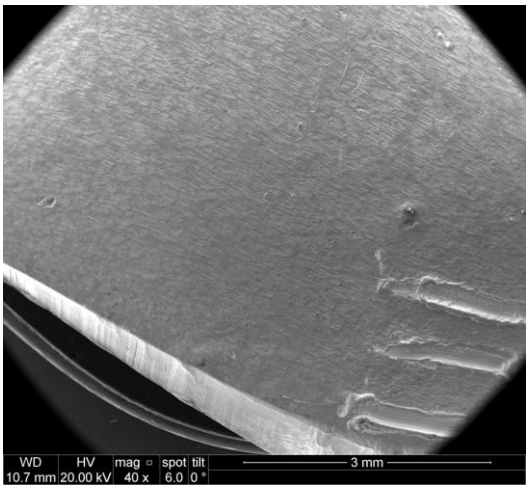
Figure 70 continued: ESEM-EDX photomicrographs of sample Pb II six months after treatment with 5 % w/v disodium EDTA in boiled deionised water at magnifications of 40x (a), 100x (b), 500x (c) and 1000x (d).



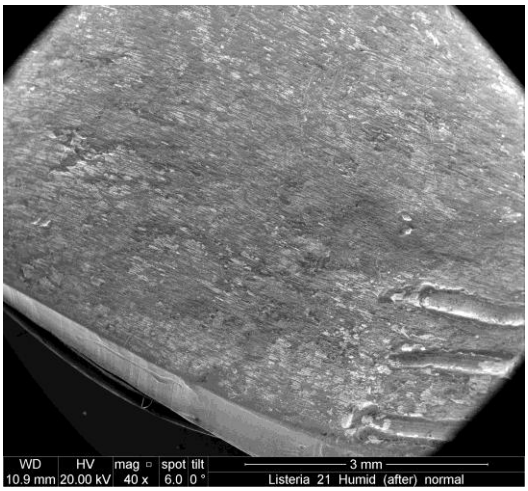
Pb III:

The ESEM photomicrographs for Pb III before and after treatment with 5 % w/v disodium EDTA in boiled deionised water made into a gel with 5 % w/v methyl cellulose at magnifications of c. 40x, 100x, 500x and 1000x are shown below. The surface of the Pb III coupon was significantly patchy after treatment at 40x magnification, and this was clearer still at higher magnifications of c. 100x, 500x and 1000x. The appearance of the lead surface suggested it had been etched, possibly due to the gel drying out since it was not covered, which may have facilitated differential aeration corrosion. The use of 5 % w/v disodium EDTA in boiled deionised water made into a gel therefore had the most pronounced visual effect on the lead surface of the three treatments analysed on the lead coupons.

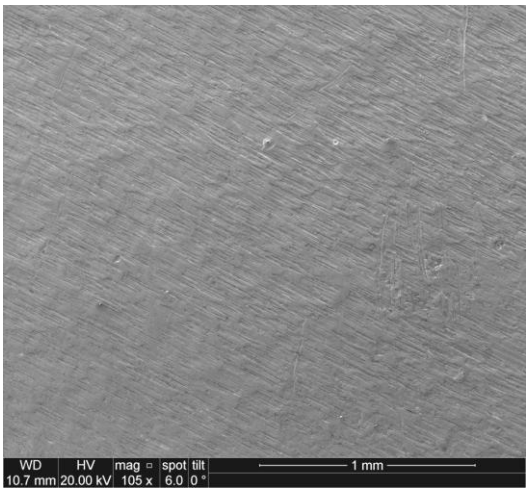
Figure 71: ESEM-EDX photomicrographs of sample Pb III before and after treatment with 5 % w/v disodium EDTA in boiled deionised water made into a gel with 5 % w/v methyl cellulose at magnifications of c. 40x, 100x, 500x and 1000x.



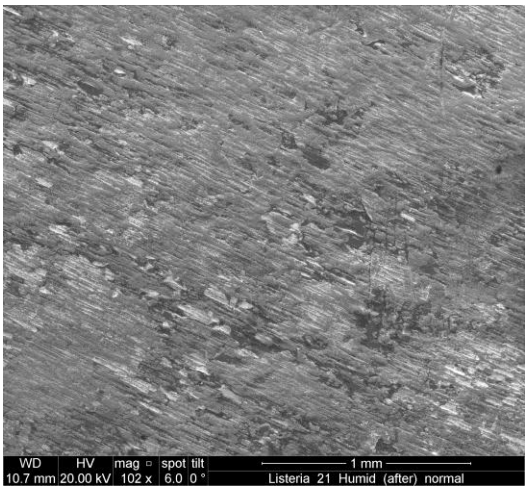
Before treatment at 40x



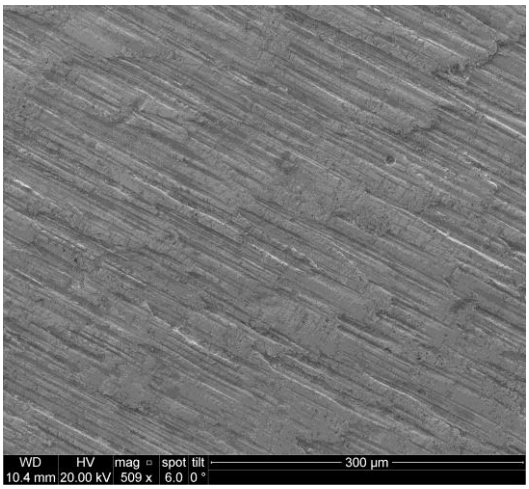
After treatment at 40x



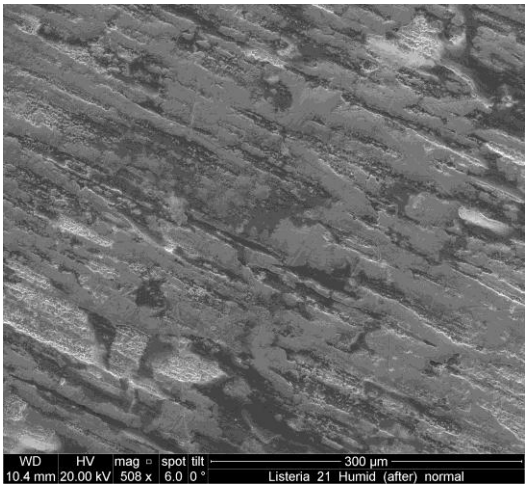
Before treatment at 105x



After treatment at 102x

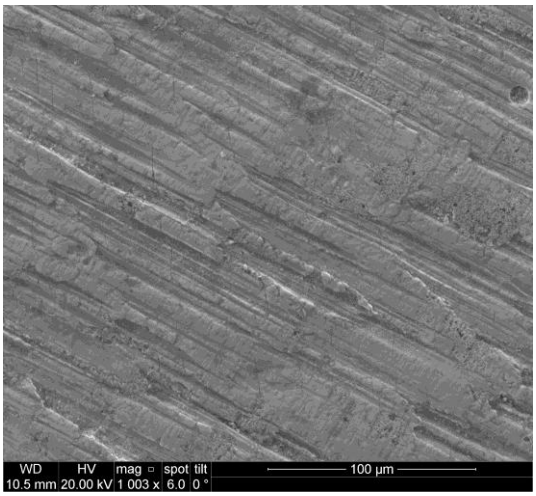


Before treatment at 509x

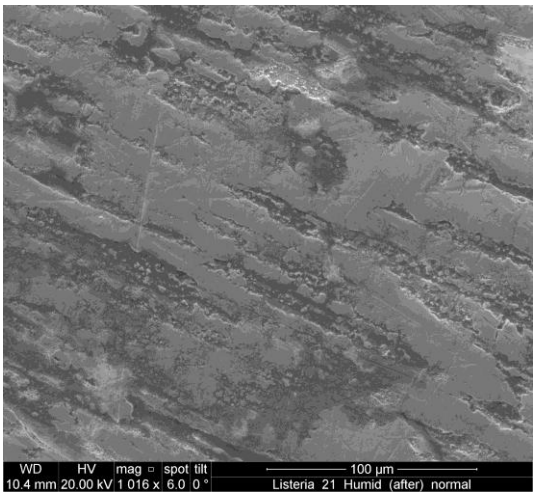


After treatment at 508x

Figure 71 continued: ESEM-EDX photomicrographs of sample Pb III before and after treatment with 5 % w/v disodium EDTA in boiled deionised water made into a gel with 5 % w/v methyl cellulose at magnifications of c. 40x, 100x, 500x and 1000x.



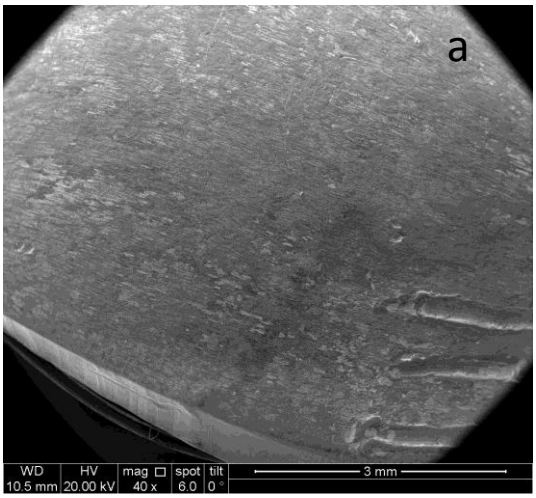
Before treatment at 1003x



After treatment at 1016x

The surface of the Pb III coupon remained patchy over time at two, four and six months after treatment, but possibly slightly less than directly after treatment, which suggests that a thin lead oxide layer may have formed. The ESEM photomicrographs of the Pb III coupon after two, four and six months at c. 40x, 100x, 500x and 1000x as follows:

Figure 72: ESEM-EDX photomicrographs of sample Pb III two months after treatment with 5 % w/v disodium EDTA in boiled deionised water made into a gel with 5 % w/v methyl cellulose at magnifications of 40x (a), 104x (b), 501x (c) and 1004x (d).



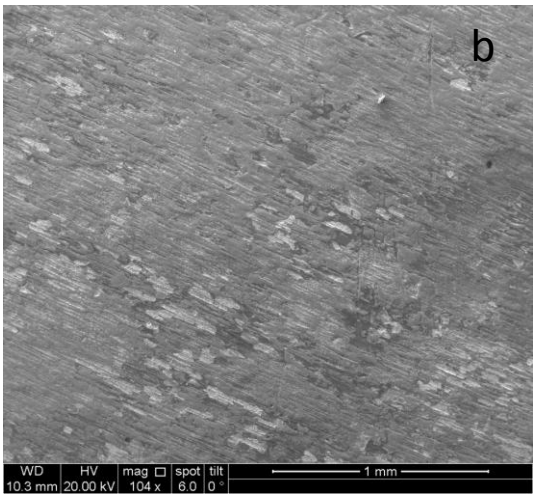


Figure 72 continued: ESEM-EDX photomicrographs of sample Pb III two months after treatment with 5 % w/v disodium EDTA in boiled deionised water made into a gel with 5 % w/v methyl cellulose at magnifications of 40x (a), 104x (b), 501x (c) and 1004x (d).

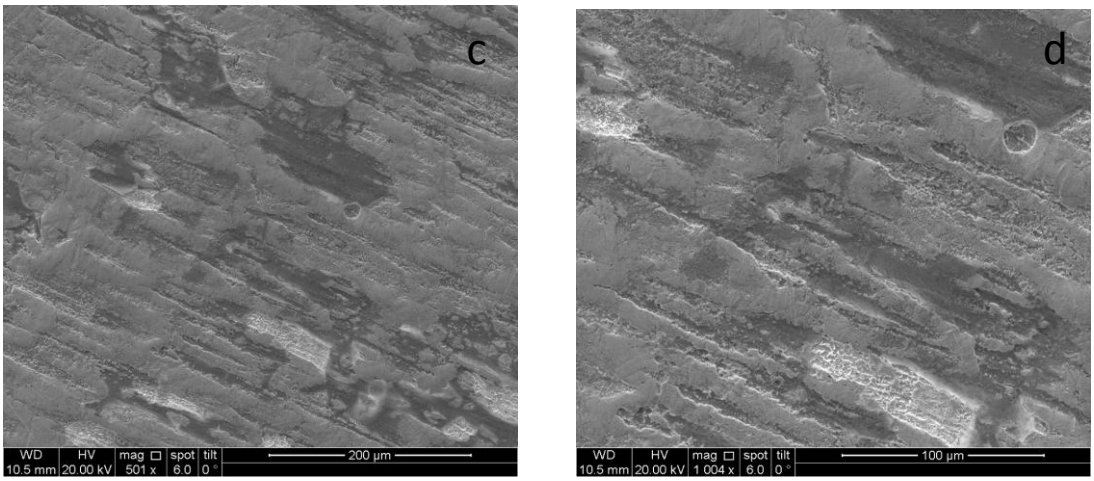


Figure 73: ESEM-EDX photomicrographs of sample Pb III four months after treatment with 5 % w/v disodium EDTA in boiled deionised water made into a gel with 5 % w/v methyl cellulose at magnifications of 40x (a), 107x (b), 501x (c) and 1006x (d).

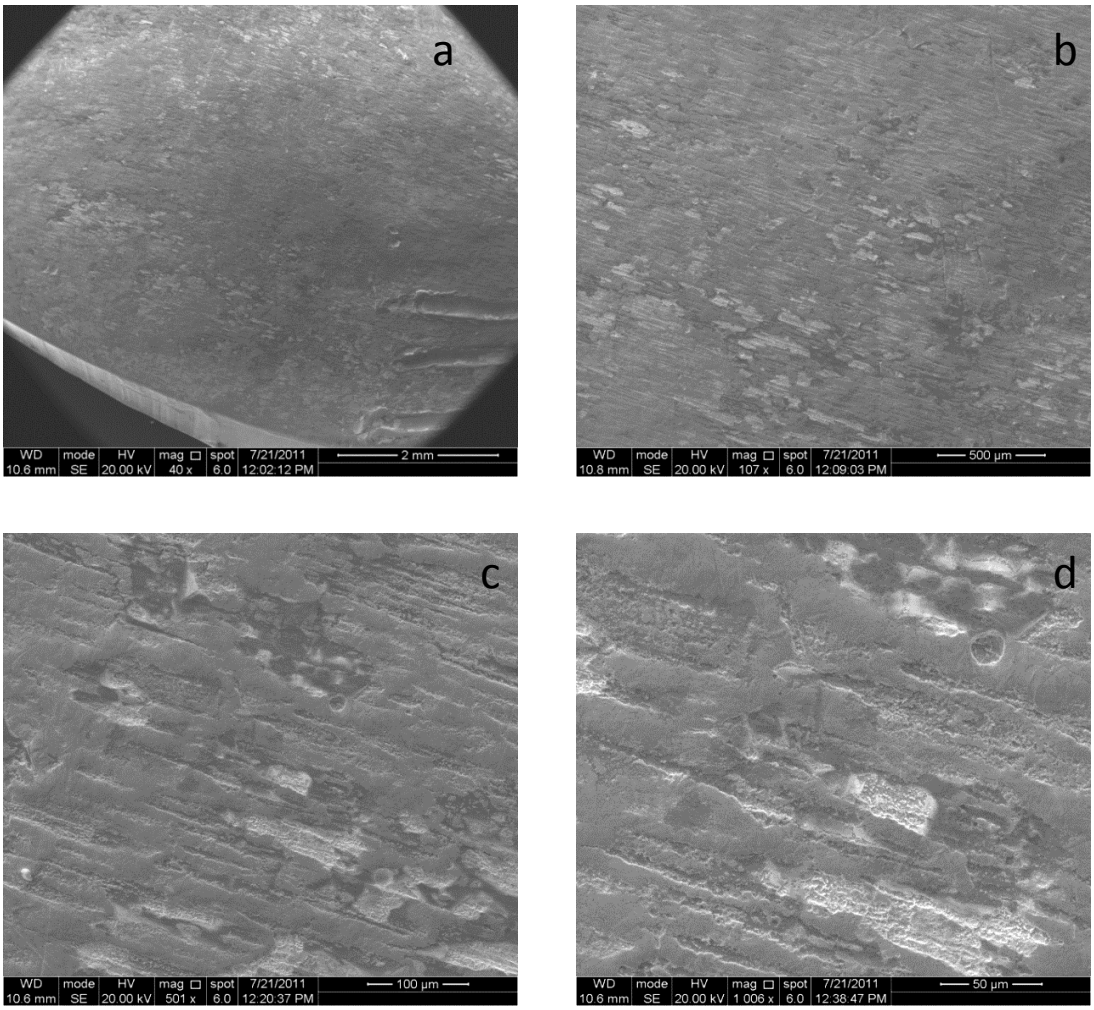
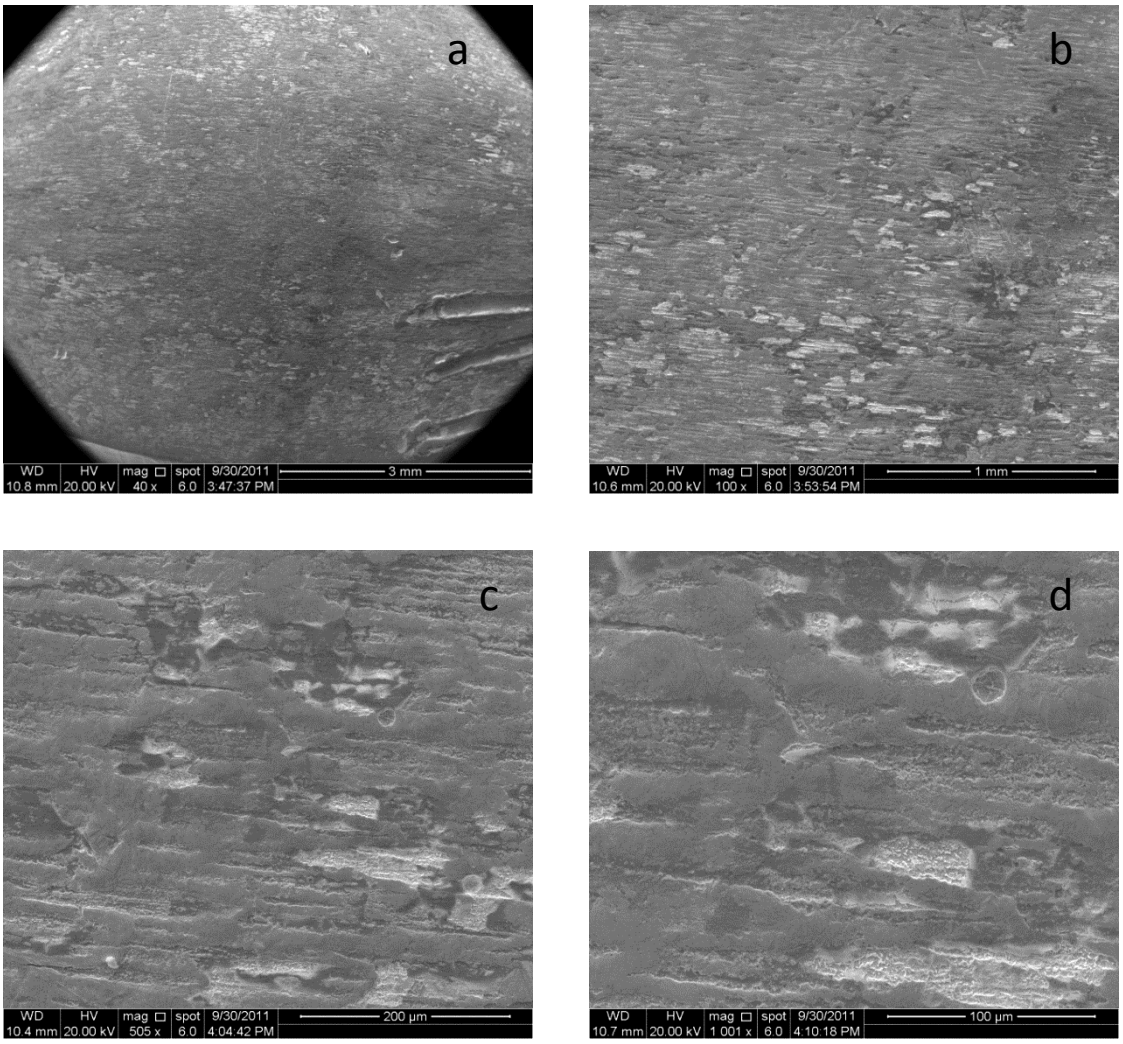


Figure 74: ESEM-EDX photomicrographs of sample Pb III six months after treatment with 5 % w/v disodium EDTA in boiled deionised water made into a gel with 5 % w/v methyl cellulose at magnifications of 40x (a), 100x (b), 505x (c) and 1001x (d).



Due to the patchy appearance of the surface of the Pb III coupon treated with 5 % w/v disodium EDTA in boiled deionised water made into a gel with 5 % w/v methyl cellulose, the EDX results for the lead coupons before and after treatment and over time after two, four and six months were compared to see if there were any significant features and the results are shown in **Table 11.**

Table 11: EDX results for Pb I, II, III coupons before (B.T.) and after treatment (A.T.) and at two, four and six months after treatment (A.T.), as well as the control IV coupon at two, four and six months.

Pb Coupon	**Pb wt. %**	**O wt. %**	**C wt. %**	**Si wt. %**
Pb I – 5 % disodium EDTA in deionised water				
Pb I - B.T.	68.3	14.8	15.1	1.86
Pb I - A.T.	81.4	5.1	13.5	-
Pb I - A.T. 2 months	78.3	7.11	14.6	-
Pb I - A.T. 4 months	80.3	9.00	10.7	-
Pb I - A.T. 6 months	78.9	10.3	10.9	-
	Pb wt. %	**O wt. %**	**C wt. %**	**Si wt. %**
Pb II - 5 % disodium EDTA in boiled deionised water				
Pb II - B.T.	65.4	16.7	16.2	1.75
Pb II - A.T.	85.7	2.90	11.4	-
Pb II - A.T. 2 months	92.6	7.44	-	-
Pb II - A.T. 4 months	80.7	8.77	10.5	-
Pb II - A.T. 6 months	75.8	12.3	12.0	-
	Pb wt. %	**O wt. %**	**C wt. %**	**Si wt. %**
Pb III - 5 % disodium EDTA in boiled deionised water in a gel				
Pb III - B.T.	64.5	18.9	16.6	-
Pb III- A.T.	79.5	6.51	14.0	-
Pb III- A.T. 2 months	75.5	10.0	14.4	-
Pb III - A.T. 4 months	76.24	10.56	13.21	-
Pb III - A.T. 6 months	75.81	12.25	11.95	-
	Pb wt. %	**O wt. %**	**C wt. %**	**Si wt. %**
Pb IV - Control				
Pb IV - A.T. 2 months	66.74	17.25	15.16	0.86
Pb IV - A.T. 4 months	68.46	18.25	12.45	0.85
Pb IV – A.T. 6 months	69.72	18.84	10.60	0.84

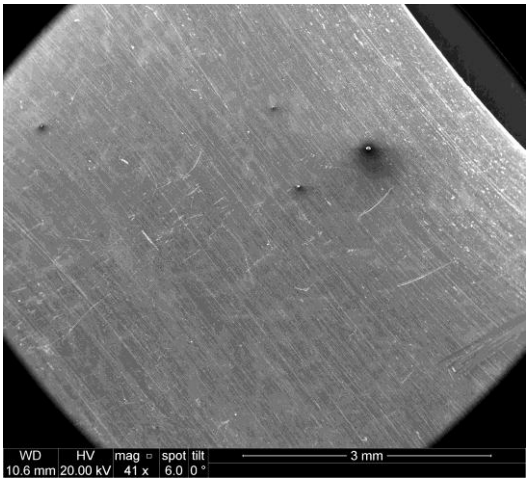
The EDX results for the lead coupons indicate that there are significantly lower wt. %s of oxygen (O) directly after treatment in all three lead coupons, and in particular with the Pb II coupon, which was treated with 5 % disodium EDTA in boiled deionised water. The oxygen levels for all three lead coupons increase over time at two, four and six months after treatment, suggesting the formation of a thin layer of lead oxide, as occurs with lead in indoor environments. This is consistent with the ESEM images, as the surface of all three lead coupons appeared to be slightly more even over time.

4.6.4 Iron Coupons

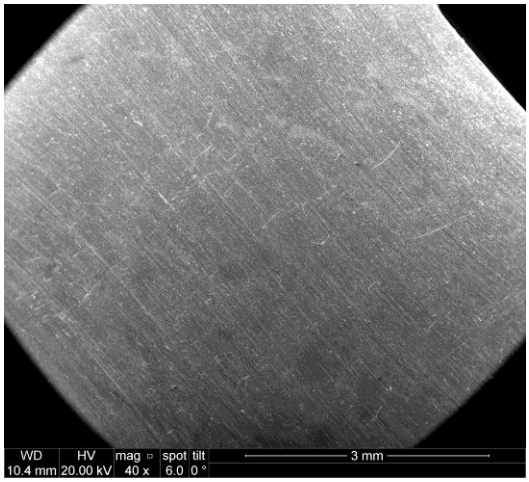
Fe I:

The ESEM photomicrographs for Fe I before and after treatment with Renaissance Metal De-Corroder at magnifications of c. 40x, 100x, 500x and 1000x are shown below. The surface of the Fe I coupon appeared to be patchy after treatment, suggesting that the iron surface had been etched, even given the somewhat uneven surface before treatment. The mottled surface of the Fe I coupon after treatment was clear without any magnification, as evident in the photograph of the metal coupons after treatment in **Figure 36.** This is not surprising as the Renaissance Metal De-Corroder contains hydro-oxycarboxilic acid and has a pH of c. 4. The iron surface appears to be cleaner after treatment, but at higher magnifications of c. 500x and 1000x it is appears slightly pitted, as there are numerous small marks in the surface that were not visible in the ESEM images at these magnifications before treatment.

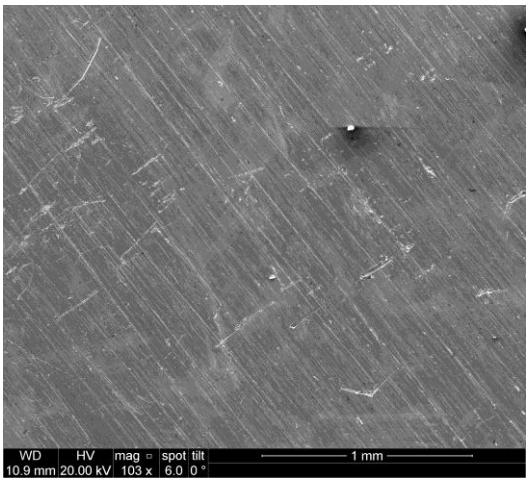
Figure 75: ESEM-EDX photomicrographs of sample Fe I before and after treatment with Renaissance Metal De-Corroder at magnifications of c. 40x, 100x, 500x and 1000x.



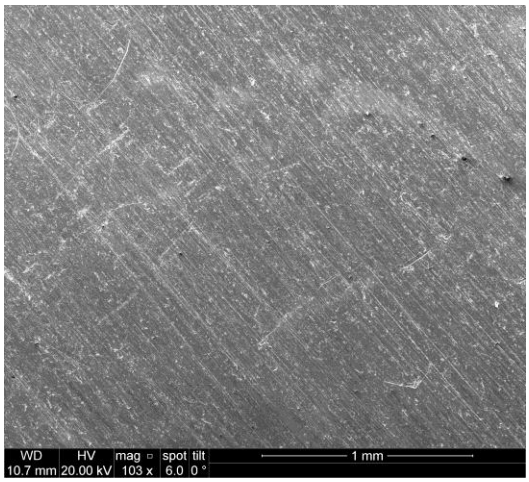
Before treatment at 41x



After treatment at 40x

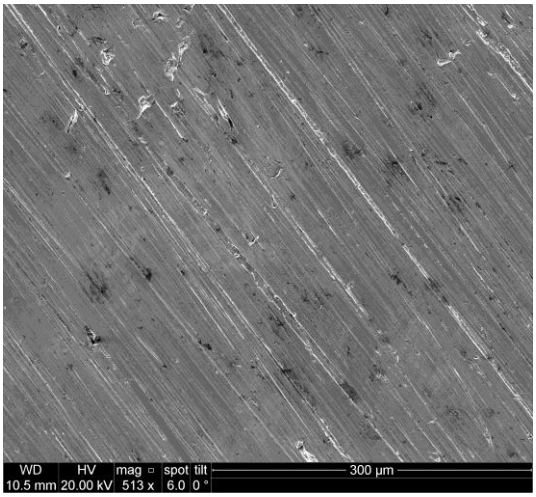


Before treatment at 103x

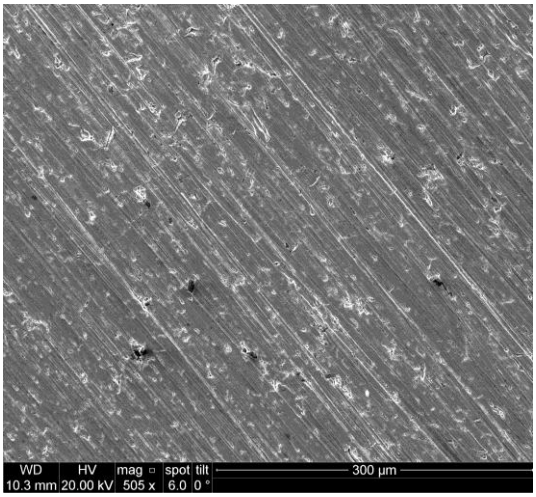


After treatment at 103x

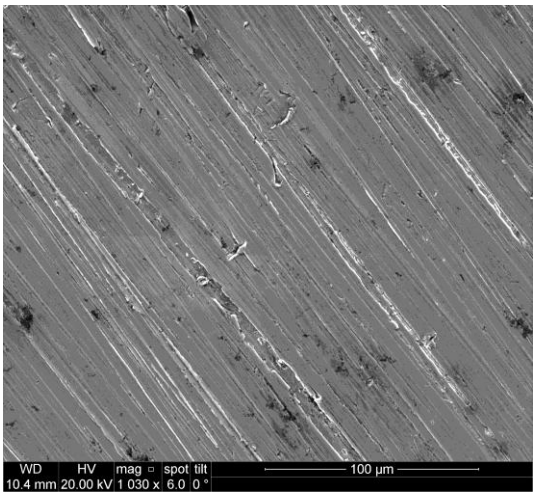
Figure 75 continued: ESEM-EDX photomicrographs of sample Fe I before and after treatment with Renaissance Metal De-Corroder at magnifications of c. 40x, 100x, 500x and 1000x.



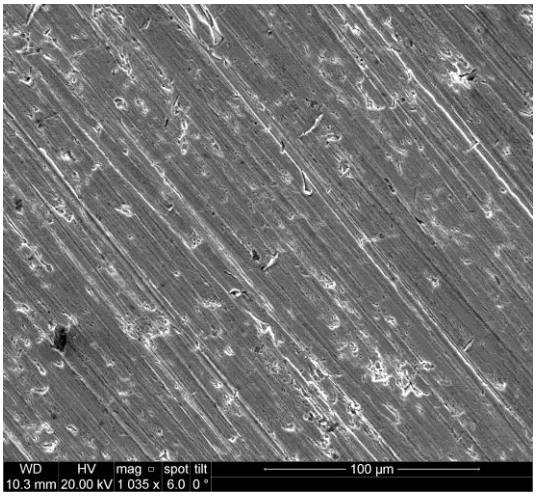
Before treatment at 513x



After treatment at 505x



Before treatment at 1030x



After treatment at 1035x

The surface of the Fe I coupon appeared to be relatively unchanged over time at two months, but appeared more patchy at lower magnifications at four and six months after treatment, suggesting the surface was reactive. The ESEM photomicrographs of the Fe I coupon after two, four and six months at magnifications of c. 40x, 100x, 500x and 1000x are as follows:

Figure 76: ESEM-EDX photomicrographs of sample Fe I two months after treatment with Renaissance Metal De-Corroder at magnifications of 40x (a), 102x (b), 503x (c) and 1034x (d).

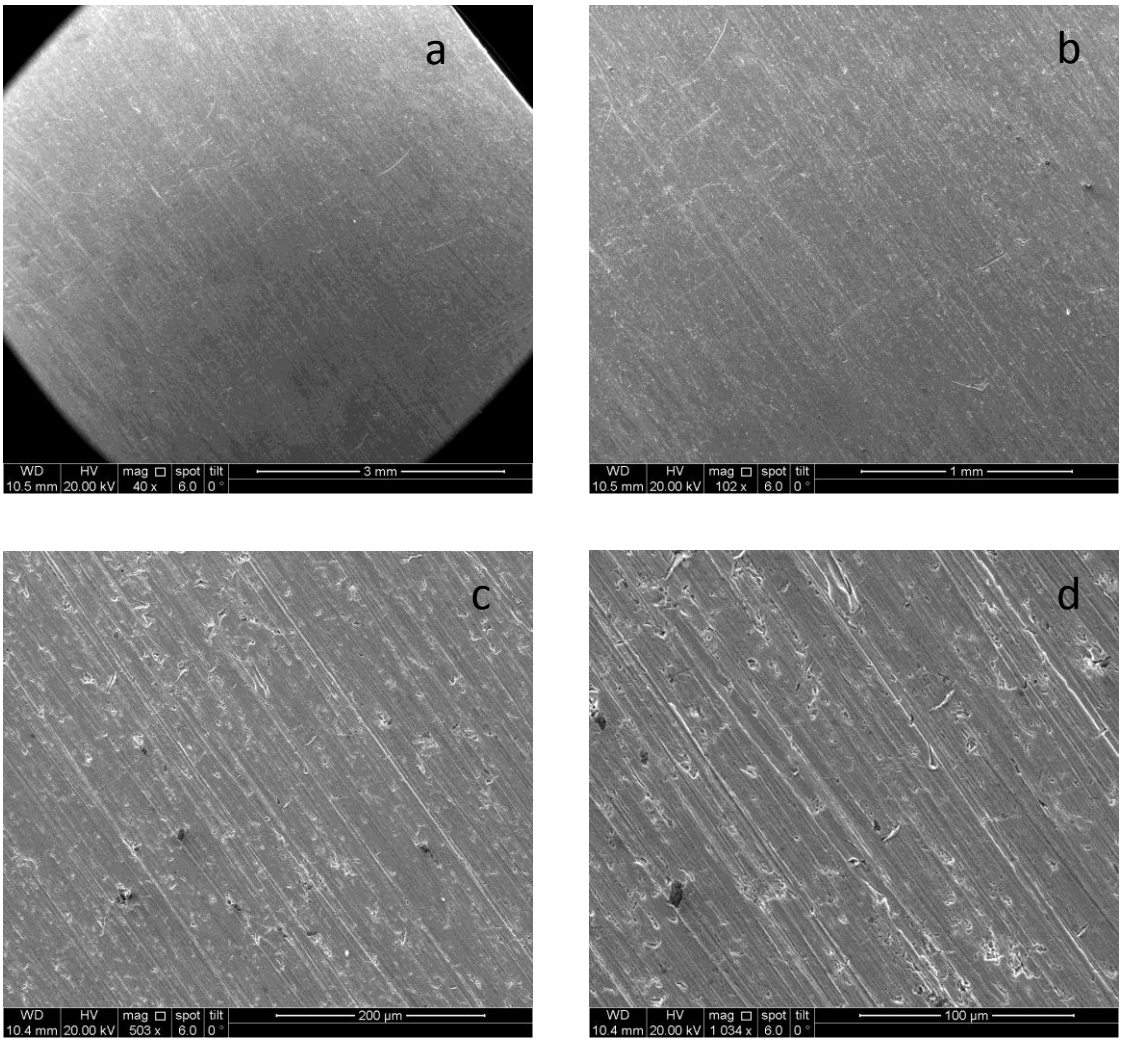


Figure 77: ESEM-EDX photomicrographs of sample Fe I four months after treatment with Renaissance Metal De-Corroder at magnifications of 40x (a), 104x (b), 505x (c) and 1012x (d).

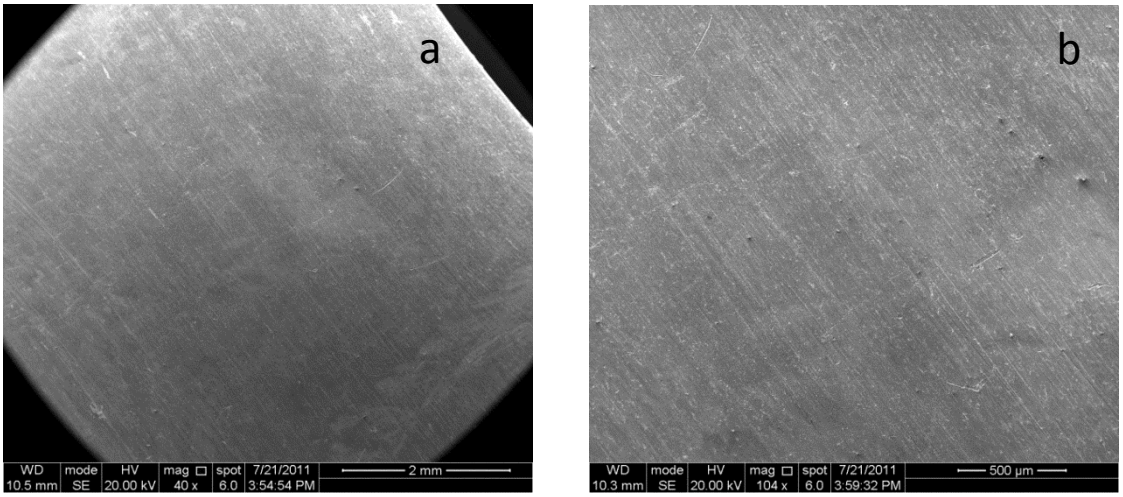


Figure 77 continued: ESEM-EDX photomicrographs of sample Fe I four months after treatment with Renaissance Metal De-Corroder at magnifications of 40x (a), 104x (b), 505x (c) and 1012x (d).

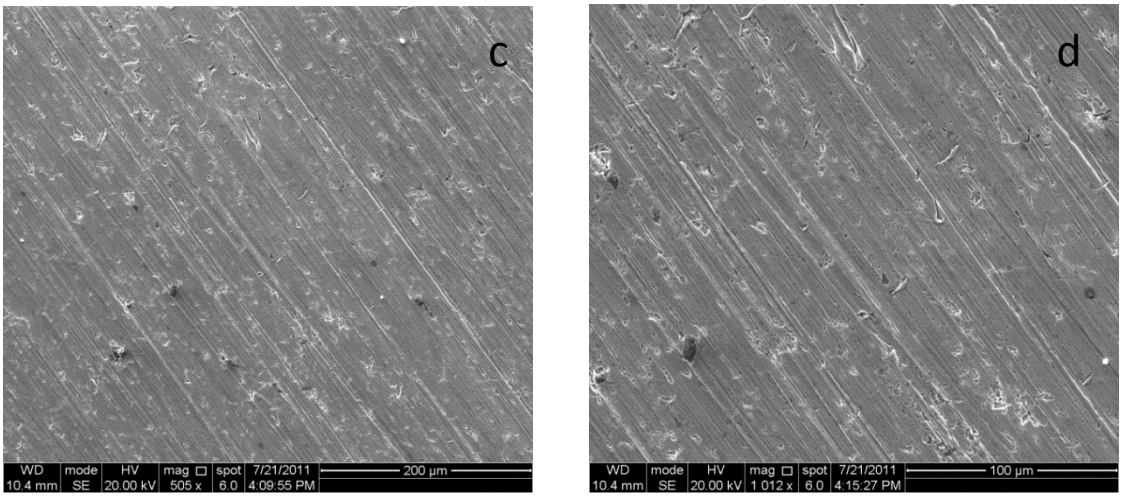
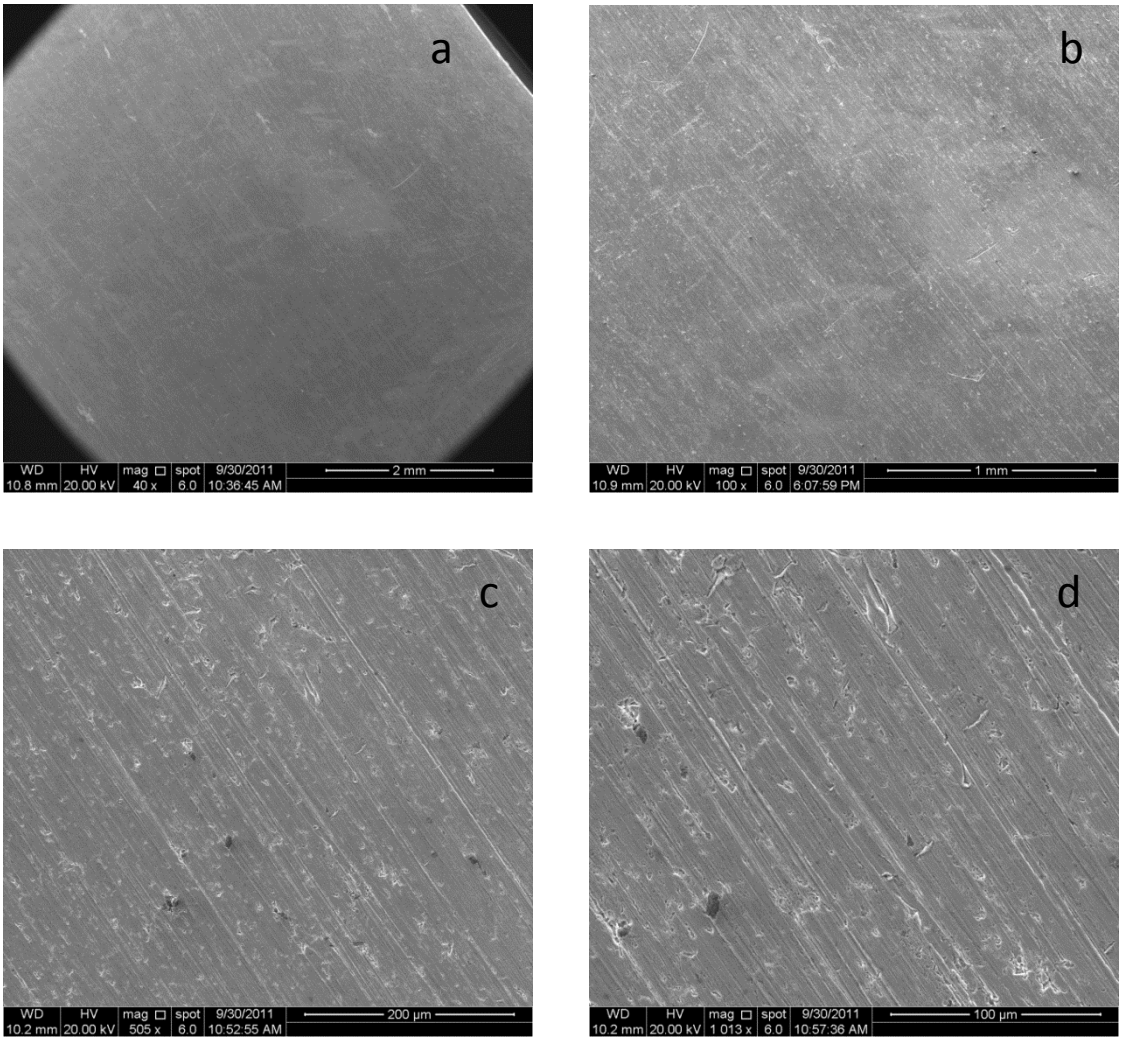


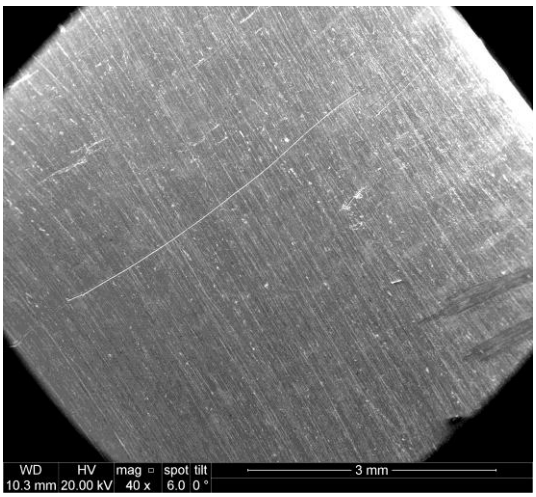
Figure 78: ESEM-EDX photomicrographs of sample Fe I six months after treatment with Renaissance Metal De-Corroder at magnifications of 40x (a), 100x (b), 505x (c) and 1013x (d).



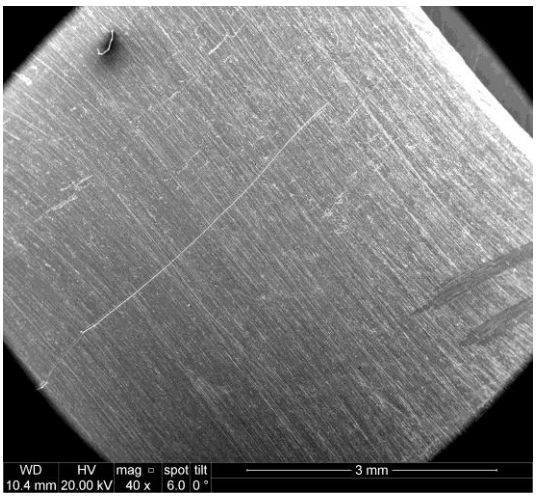
Fe II:

The ESEM photomicrographs for Fe II before and after treatment with Pre-Lim Surface Cleaner at magnifications of c. 40x, 100x, 500x and 1000x are shown below. The surface of the Fe II coupon appeared to be relatively unchanged after treatment. There were no new scratches visible and the iron surface had a slightly cleaner, polished appearance, for example at c. 500x magnifications. The Pre-Lim Surface Cleaner therefore appeared to be the mildest of the three iron cleaning treatments analysed.

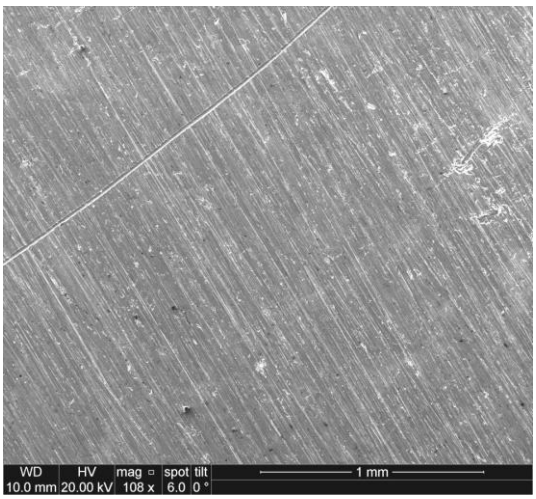
Figure 79: ESEM-EDX photomicrographs of sample Fe II before and after treatment with Pre-Lim Surface Cleaner at magnifications of c. 40x, 100x, 500x and 1000x.



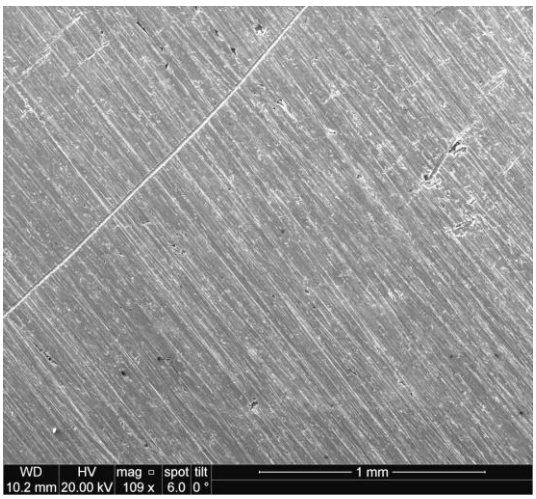
Before treatment at 40x



After treatment at 40x

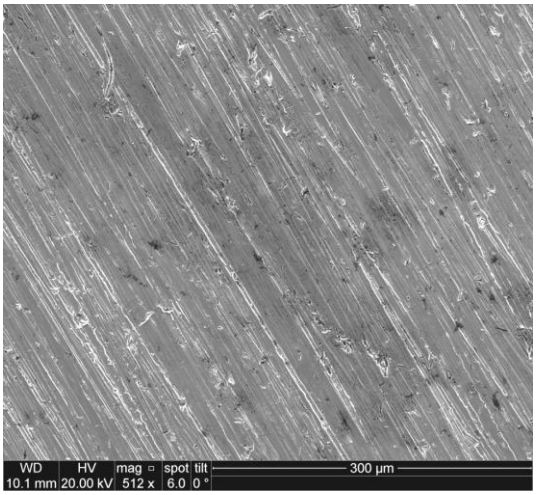


Before treatment at 108x

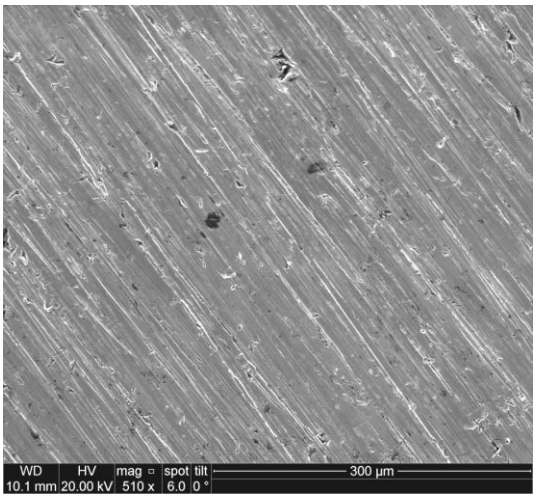


After treatment at 109x

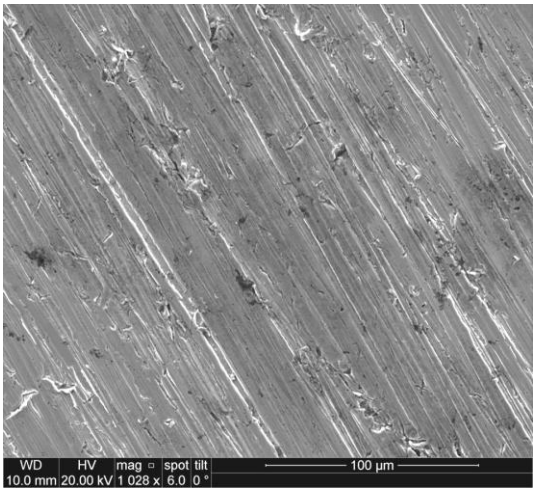
Figure 79 continued: ESEM-EDX photomicrographs of sample Fe II before and after treatment with Pre-Lim Surface Cleaner at magnifications of c. 40x, 100x, 500x and 1000x.



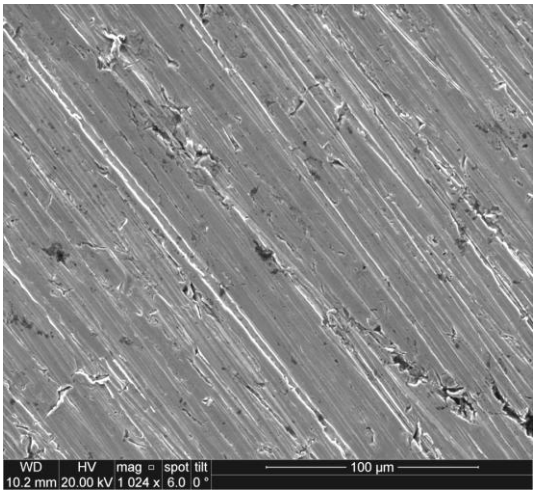
Before treatment at 512x



After treatment at 510x



Before treatment at 1028x



After treatment at 1024x

The surface of the Fe II coupon appeared to be unchanged over time at two, four and six months, suggesting that the iron surface was relatively stable after treatment. The ESEM photomicrographs of the Fe II coupon after two, four and months at c. 40x, 100x, 500x and 1000x are as follows:

Figure 80: ESEM-EDX photomicrographs of sample Fe II two months after treatment with Pre-Lim Surface Cleaner at magnifications of 40x (a), 101x (b), 510x (c) and 1014x (d).

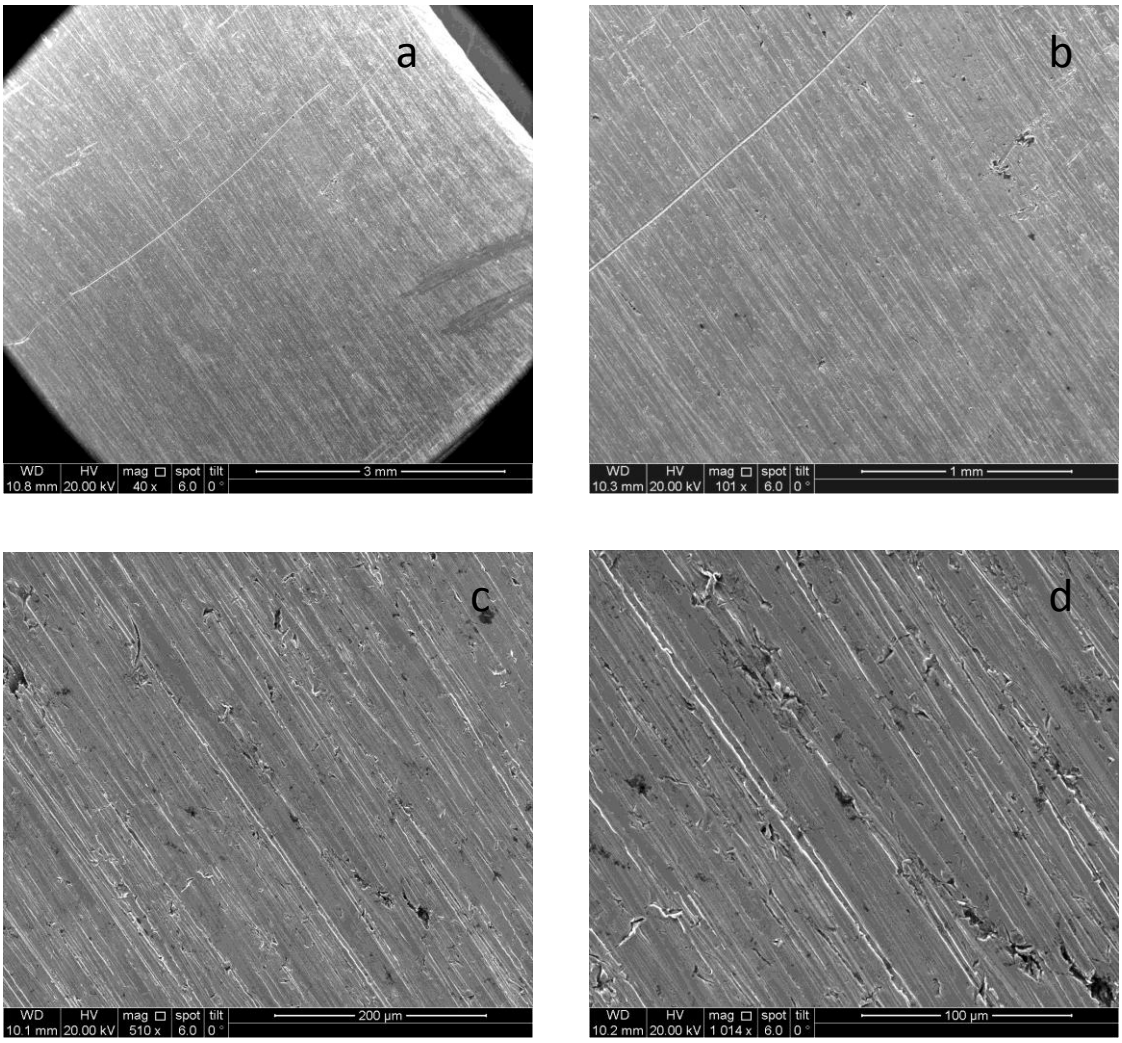


Figure 81: ESEM-EDX photomicrographs of sample Fe II four months after treatment with Pre-Lim Surface Cleaner at magnifications of 40x (a), 102x (b), 515x (c) and 1014x (d).

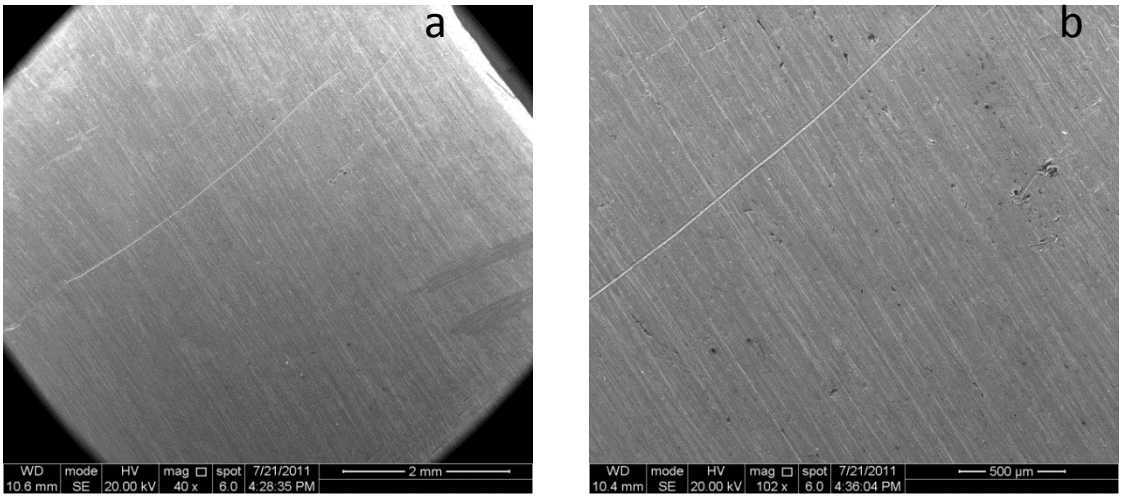


Figure 81 continued: ESEM-EDX photomicrographs of sample Fe II four months after treatment with Pre-Lim Surface Cleaner at magnifications of 40x (a), 102x (b), 515x (c) and 1014x (d).

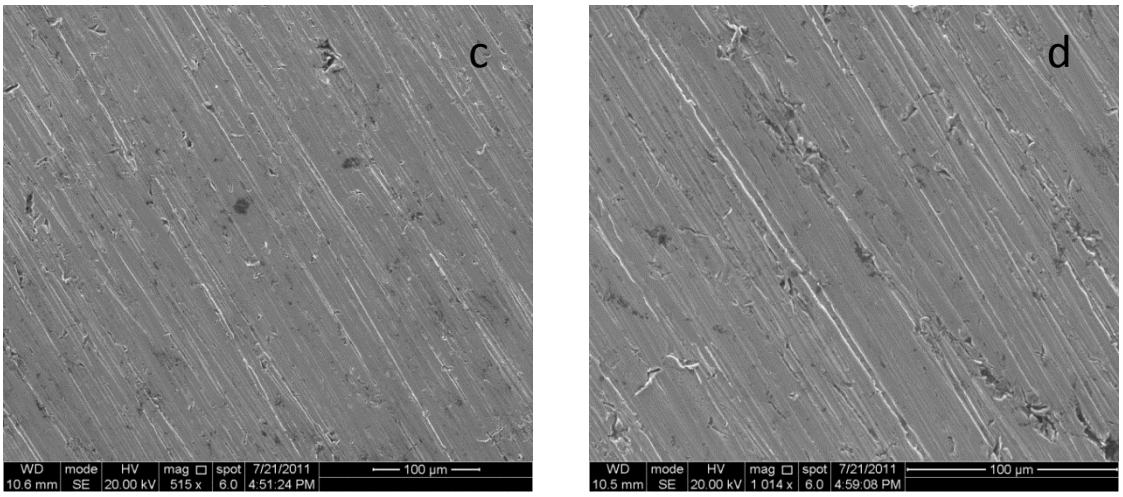
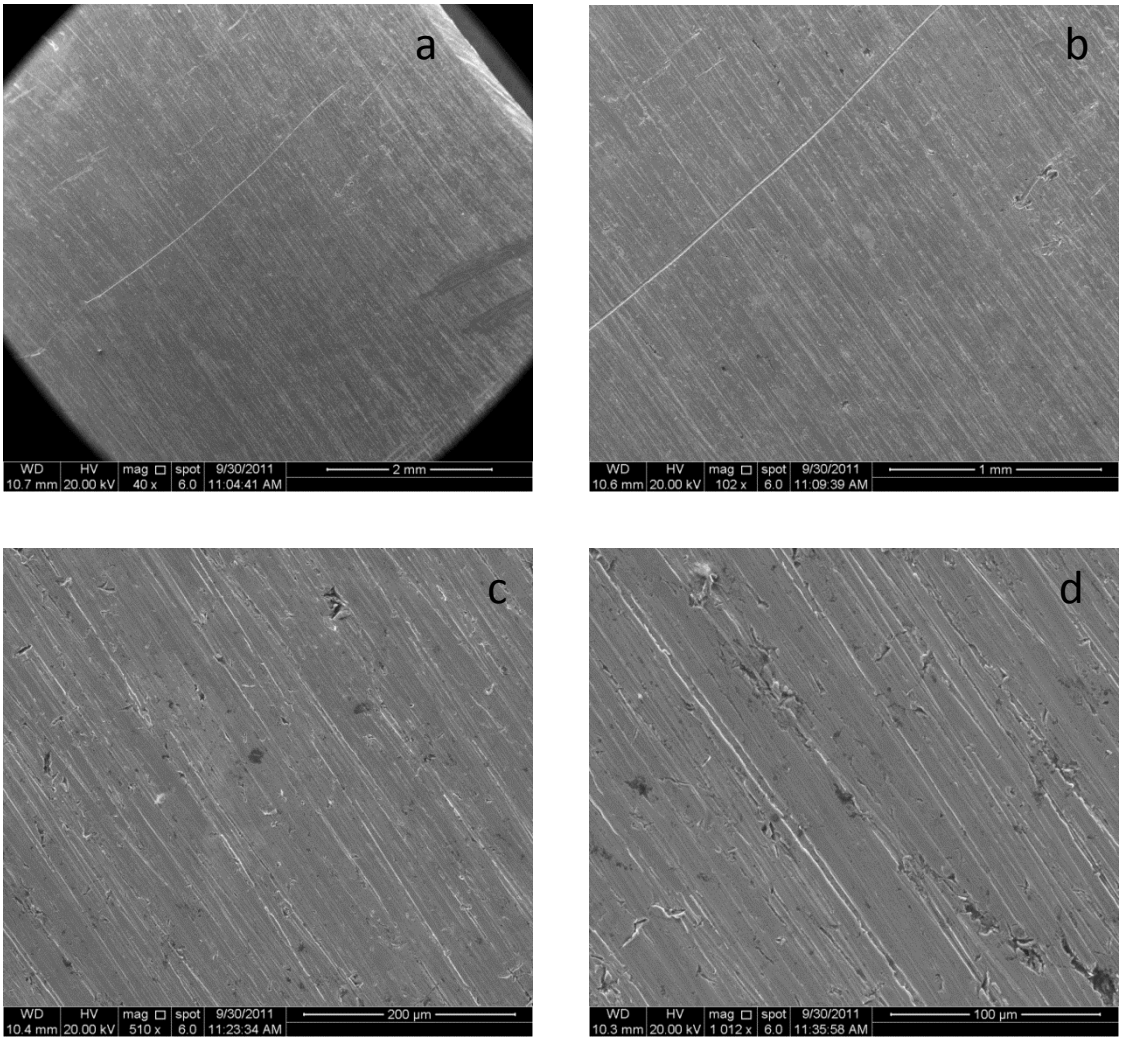


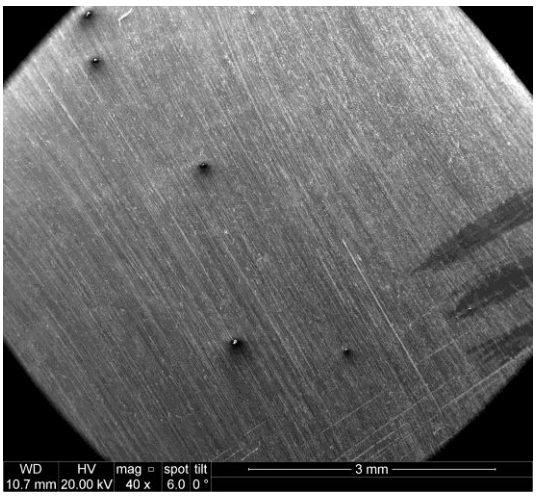
Figure 82: ESEM-EDX photomicrographs of sample Fe II six months after treatment with Pre-Lim Surface Cleaner at magnifications of 40x (a), 102x (b), 510x (c) and 1012x (d).



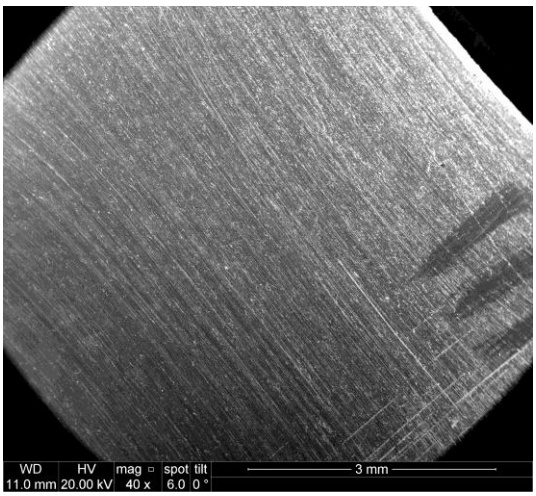
Fe III:

The ESEM photomicrographs for Fe III before and after treatment with Nevr Dull Wadding Polish at magnifications of c. 40x, 100x, 500x and 1000x are shown below. The surface of the Fe III coupon appeared to be more even and slightly polished after treatment, in that imperfections and minor scratches appear to have been reduced. There are no new scratches visible and the surface looks cleaner at the higher magnifications of c. 100x, 500x and 1000x. The Nevr Dull Wadding Polish therefore appears to be a more suitable surface cleaning treatment for iron than for copper.

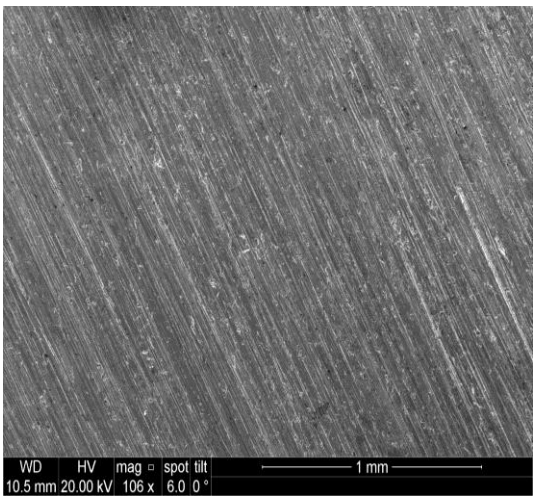
Figure 83: ESEM-EDX photomicrographs of sample Fe III before and after treatment with Nevr Dull Wadding Polish at magnifications of c. 40x, 100x, 500x and 1000x.



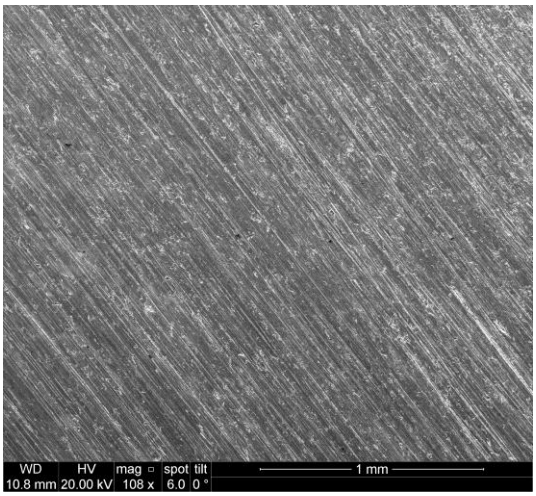
Before treatment at 40x



After treatment at 40x

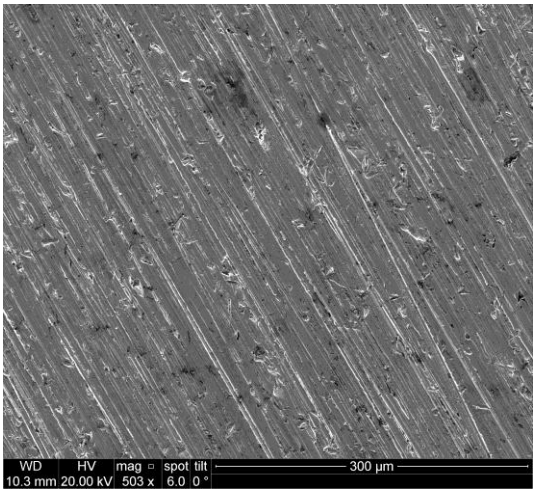


Before treatment at 106x

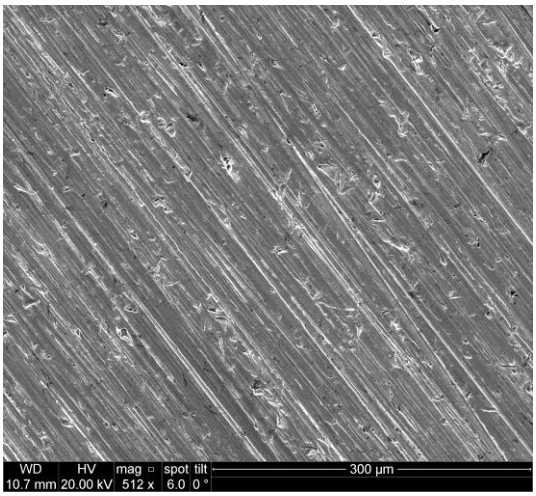


After treatment at 108x

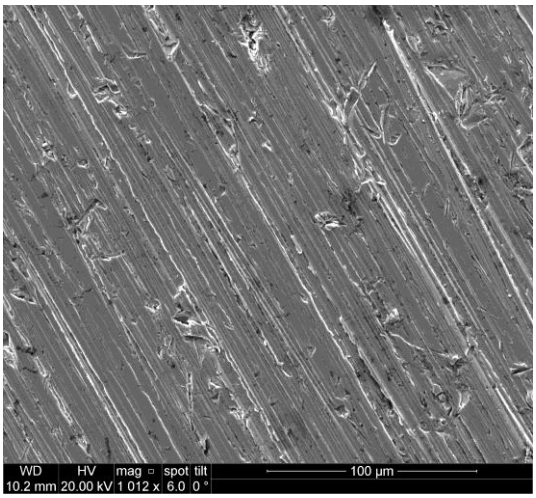
Figure 83 continued: ESEM-EDX photomicrographs of sample Fe III before and after treatment with Nevr Dull Wadding Polish at magnifications of c. 40x, 100x, 500x and 1000x.



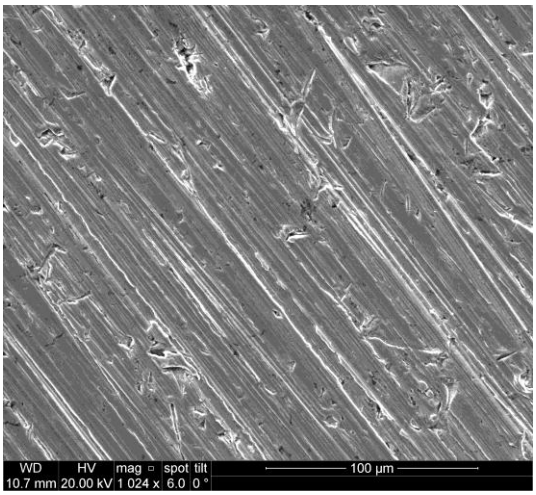
Before treatment at 503x



After treatment at 512x



Before treatment at 1012x



After treatment at 1024x

The surface of the Fe III coupon appeared to be relatively unchanged over time at two, four and six months, suggesting that the iron surface was stable after treatment. The ESEM photomicrographs of the Fe III coupon after two, four and six months at c. 40x, 100x, 500x and 1000x are as follows:

Figure 84: ESEM-EDX photomicrographs of sample Fe III two months after treatment with Nevr Dull Wadding Polish at magnifications of 40x (a), 107x (b), 503x (c) and 1010x (d).

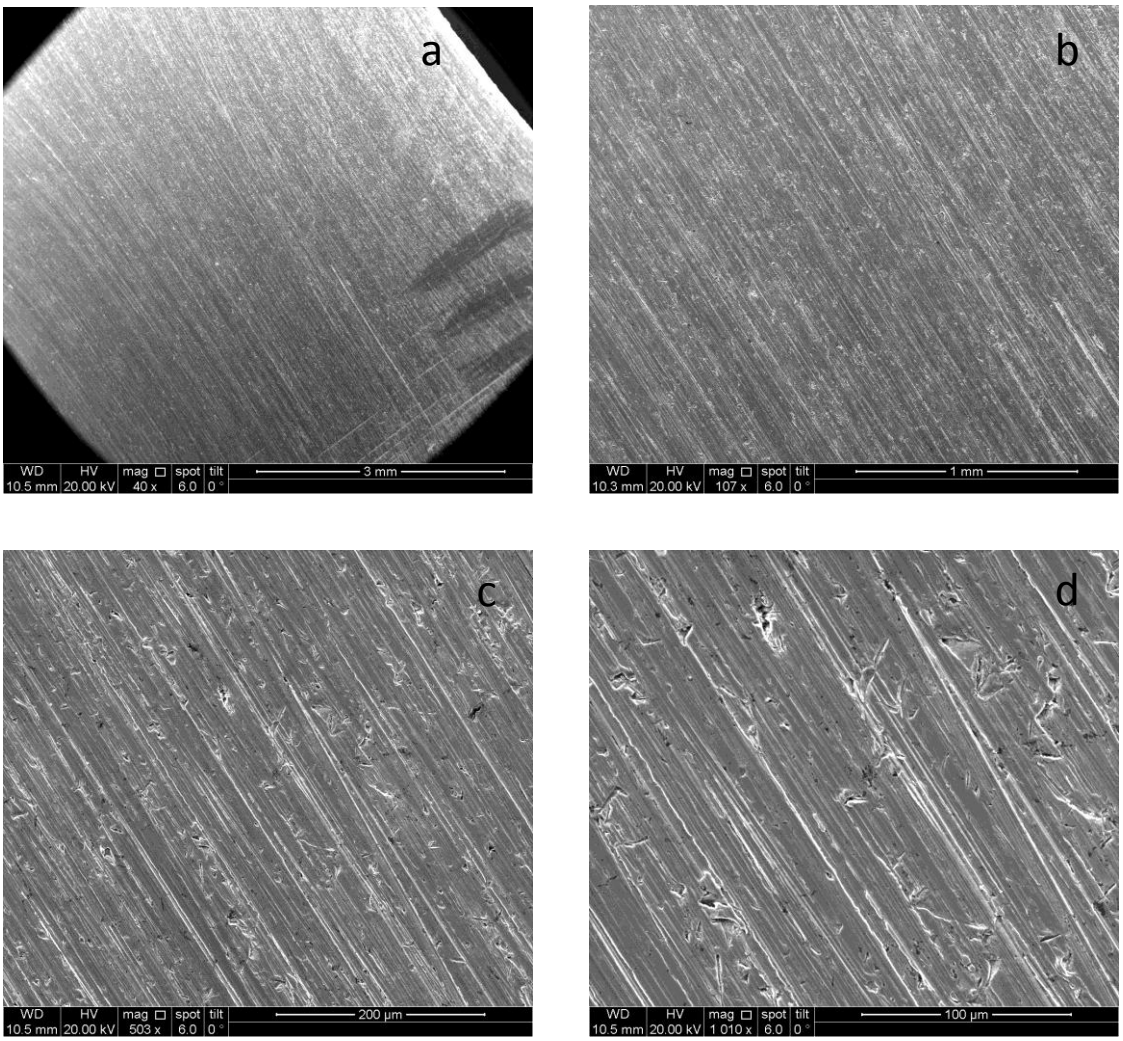


Figure 85: ESEM-EDX photomicrographs of sample Fe III four months after treatment with Nevr Dull Wadding Polish at magnifications of 40x (a), 102x (b), 508x (c) and 1000x (d).

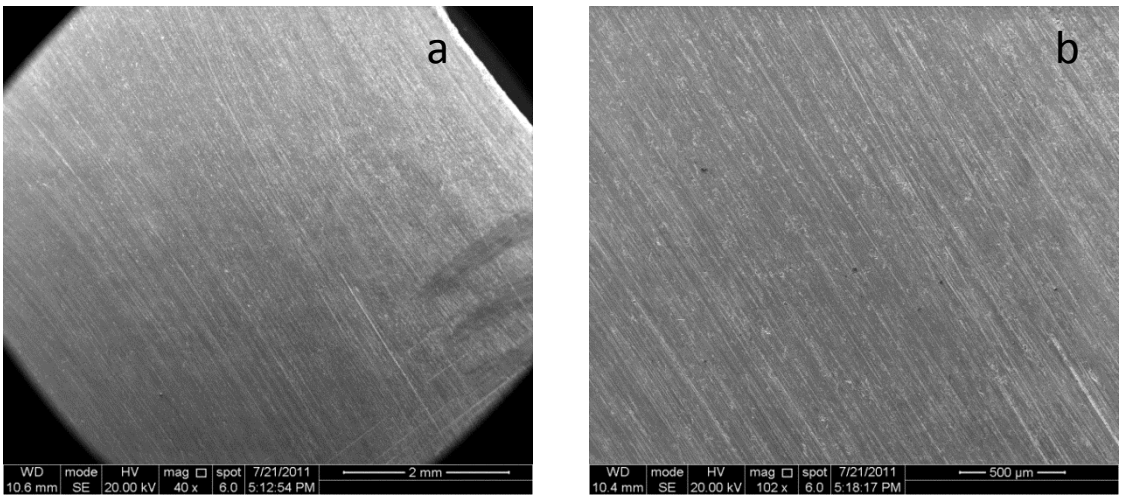


Figure 85 continued: ESEM-EDX photomicrographs of sample Fe III four months after treatment with Nevr Dull Wadding Polish at magnifications of 40x (a), 102x (b), 508x (c) and 1000x (d).

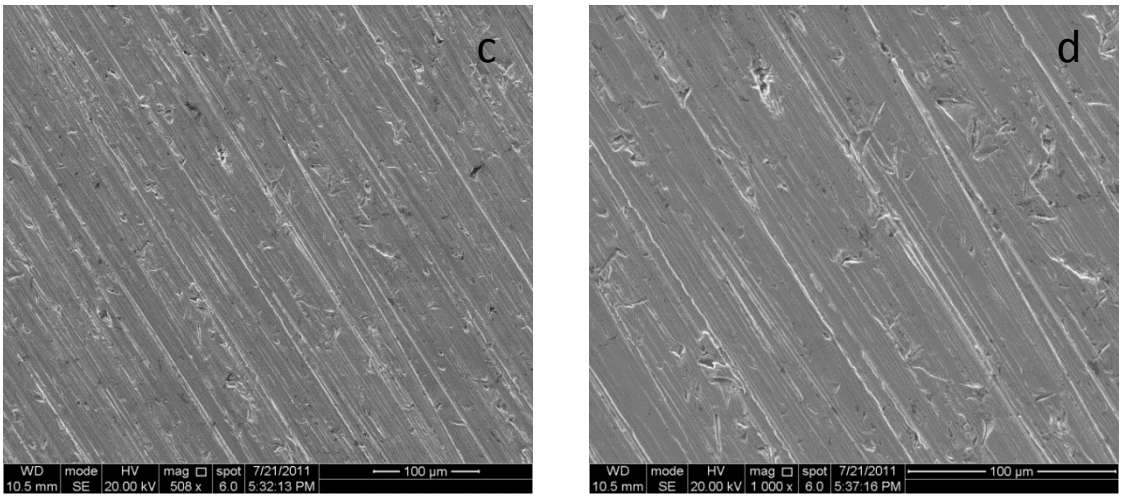
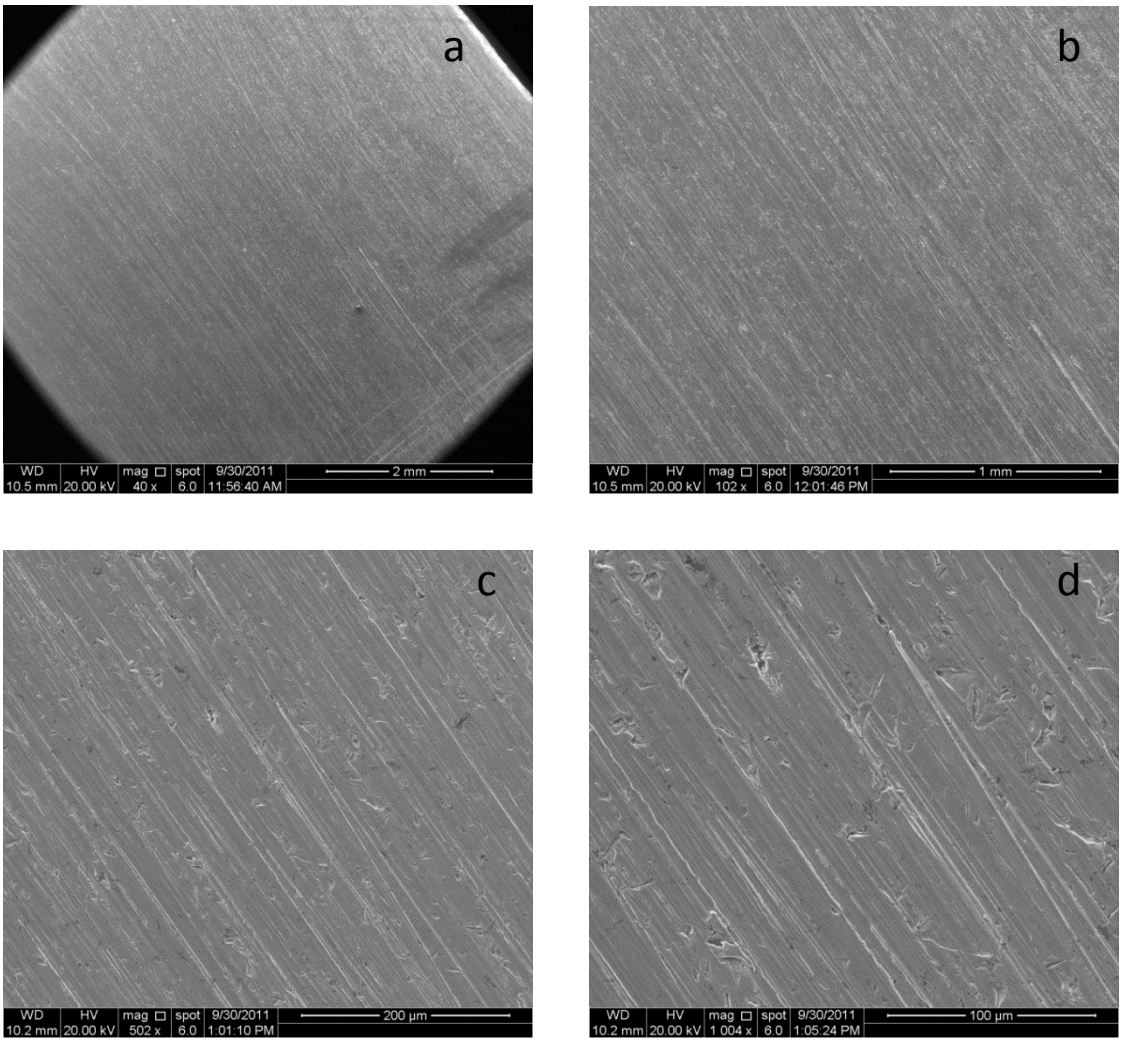


Figure 86: ESEM-EDX photomicrographs of sample Fe III six months after treatment with Nevr Dull Wadding Polish at magnifications of 40x (a), 102x (b), 502x (c) and 1004x (d).



4.7 Conclusions

The ESEM-EDX analysis of the six proprietary products and four conservation preparations provided useful information on the effects of these chemical and abrasive cleaning treatments for the silver, copper, lead and iron coupons, which can be incorporated into the decision making process in metals conservation, in particular for historic metal objects. The ESEM images were consistent and contribute to a visual database or atlas of the effects of cleaning treatments in metals conservation, which could be used as a reference to complement the information in materials safety data sheets for proprietary products and the materials in conservation preparations. The ESEM-EDX results demonstrated that all the cleaning treatments tested had some effect on the surface of the bare metals coupons, even the relatively mild abrasive treatments such as the precipitated calcium carbonate in a paste with ethanol for cleaning silver. This is useful for the conservation of objects with components made of the metals analysed, particularly those with bare metal surfaces in combination with tarnished or corroded areas that require treatment. In the treatment of tarnished or corroded historic metal objects the clean metal can be exposed at different rates over the surface of objects, therefore an understanding of the effects of the materials and techniques used to treat the tarnished or corroded areas, on the adjacent areas of bare or clean metal is important. Particularly if the proprietary products or conservation preparations do not contain corrosion inhibitors designed to protect the clean metal surfaces as they are exposed during treatment.

This also applies to the conservation of some metal objects from anthropological and archaeological contexts that have bare metal surfaces or a combination of bare metal and tarnished or corroded areas. For example, objects that have been cleaned back to bare metal in the past and given uneven surface coatings such as lacquer or surface coatings such as lacquer that have deteriorated, which has led to preferential tarnish and corrosion of the exposed metal areas. The removal of corrosion products or ‘stripping’ of metal objects was carried out in the conservation of metal objects in the past, and while this needs to be considered in the context of the development of the conservation profession, it has led to objects with clean metal surfaces or combinations of clean metal areas and re- tarnished or re-corroded areas that require treatment. In some cases it has led to over-cleaning of the objects, where the materials or techniques used have caused pitting or etching of the clean metal surfaces uncovered during treatment, for example when they haven’t been protected by corrosion inhibitors. The use of cleaning treatments that leave residues can also result in metal objects having clean metal areas in combination with re-tarnished or re-corroded areas that require treatment. There are also metal objects that are regularly cleaned such as

collections of decorative silver objects exhibited in historic houses and period rooms, as well as Navajo silver jewellery to show how the objects would appear when in use and as a sign of respect for the objects.

By following a systematic procedure in the application of the cleaning treatments as well as in the ESEM-EDX analyses it was possible to see significant changes or the absence of them in the ESEM-EDX results. Some of the changes were visible in the ESEM images at magnifications of c. 40x, which is useful information, as it indicates that the types of microscopes found in conservation laboratories and conservation training programmes with magnifications up to c. 60-70x could be used to examine the effects of interventive cleaning treatments for metal objects. This could be done as a preliminary step before further analysis if there was access to analytical equipment such as the ESEM-EDX, as the ESEM images at higher magnifications provided additional detailed information, such as indicating scratching and fine pitting of the metal surfaces, as well as surface deposits that may be residues of the cleaning treatments which were not as visible at the lower magnifications.

The ESEM-EDX analyses demonstrated that two of the most important factors to assess before cleaning treatments are carried out on metal objects are the pH of the components in chemical treatments and the hardness of abrasive materials in the mechanical treatments compared with the hardness of the metal being treated. For example the ESEM images of the metal surface after treatment with the acidic proprietary products Goddard's Silver Dip (pH < 2), Liberon Brass and Copper Polish (pH 2.4) and Renaissance Metal De-Corroder (pH c. 4) indicated that the metal had been etched. As did the ESEM images for the conservation preparation of 5 % w/v disodium EDTA in boiled deionised water made into a gel with 5 % w/v methyl cellulose (pH 4.5), and left uncovered on the lead coupon. This was significant as not all gels are covered during treatment, sometimes due to the awkward shape or size of the objects being treated. While the use of the alkaline proprietary product Silvo Silver Dip, which contains ammonia, appeared to result in fine surface pitting visible at higher magnifications of c. 500 and 1000x.

In comparison the mechanical treatments involving the use of abrasives such as precipitated calcium carbonate in a paste with ethanol for cleaning silver, Pre-Lim Surface Cleaner for cleaning copper and iron and Nevr Dull Wadding for cleaning iron did not result in significant negative changes in the surface of the metal coupons. The ESEM-EDX results indicated that the use of abrasive materials left the surface of the metal coupons less reactive than those treated with the acidic and alkaline chemical proprietary products and conservation preparations. This

was evident in the ESEM images over time at two, four and six months, as the surfaces of the metal coupons treated with abrasive cleaning techniques remained relatively unchanged or stable during this period.

The results are therefore consistent with the published literature on cleaning treatments in metals conservation discussed earlier, as proprietary products in general and treatments involving the use of highly acidic or alkaline chemical components and such as acidified thiourea or ammonia, as well as relatively aggressive abrasives are not recommended for use in metals conservation (North, 1980; Wharton et al., 1990; Selwyn and Costain, 1991; Bishop Museum, 1996; Selwyn, 1997, 1999 and 2004). The consequences of inadequate rinsing of the chemicals and materials used in cleaning treatments are also illustrated in the ESEM results, for example in the residues apparent after the use of the 5 % w/v disodium EDTA in deionised water on the Pb I lead coupon. EDX analysis of part of the dark rimmed deposit on the Pb I coupon after treatment with this solution indicated sodium, calcium and potassium, as well as lead, oxygen, carbon and silicon which were identified in the lead control coupon IV. The sodium could be due to residues from the disodium EDTA, while further analysis is required to investigate the presence of the calcium and potassium. In addition, the ESEM results indicated that there can be side effects in the use of recommended treatments such as precipitated calcium carbonate in a paste with ethanol for cleaning silver, as there was fine scratching in the surface of the Ag III coupon, visible at the higher magnifications of c. 500 and 1000x. This is also consistent with conservation literature on the cleaning of historic silver objects (Selwyn, 1999).

Therefore the indiscriminate application of proprietary products and conservation preparations such as those tested is not recommended, in particular the use of cleaning treatments including highly acidic or alkaline components and aggressive abrasives. The results of the ESEM-EDX analyses however indicated that if the effects of proprietary products are systematically analysed before use, some may be considered safe to use in the controlled treatment of certain types of historic metals objects, as well as certain types of anthropological objects, with bare metal surfaces or thin layers of tarnish on the surface. Of the proprietary products and conservation preparations analysed, the cleaning treatments that showed the least damaging effects on the metal coupons tested are as follows:

Silver: Precipitated calcium carbonate in a paste with ethanol

Copper: Pre-Lim Surface Cleaner

Lead: 5 % w/v disodium EDTA in boiled deionised water – rinsed thoroughly

Iron: Pre-Lim Surface Cleaner followed by Nevr Dull Wadding Polish

The application of cleaning treatments in metals conservation however involves a number of other factors in addition to understanding the effects of the materials and techniques used to treat the objects. An assessment of the ethics of cleaning the metal object(s) is essential, including an awareness of the cultural context of the object(s) and the intent of the cultural group who made and/or used them, as well as the manufacturing techniques and the history of the object(s) use; consideration of whether cleaning is necessary for the context in which the object(s) will be displayed, sent on loan, stored or examined for research purposes and discussion with the curators or owners of the object(s) requesting the conservation work. The use of interventive cleaning treatments such as those tested may not be necessary. If the metal object(s) are stable it may be ethical and beneficial for the object(s) not to clean them, as cleaning treatments are not reversible and remove varying amounts of metal from the surface each time they are carried out. The extent of the cleaning is another factor to consider. Investigative cleaning may be a more appropriate approach to take, and the trend towards investigative cleaning in the conservation of archaeological metal objects, as documented by English Heritage (2008), may be applicable in the conservation of other types of metal objects from historic and anthropological contexts. Given that it is possible to learn more about an object during its conservation, an advantage of a more controlled, minimal approach such as investigative cleaning is that the treatment can be evaluated and modified if necessary as it is being carried out (Caple, 2000: 99).

If cleaning is considered necessary after a detailed assessment and documentation of the condition of the object(s), its manufacture, cultural context and intended context or use has been carried out, a customized approach is recommended where object(s) is treated on an individual basis. The extent of the tarnish or corrosion and any physical forms deterioration such as broken or unstable parts need to be taken into account, as well as how effective the proposed cleaning treatment is at removing or reducing the tarnish, corrosion products or surface deposits and the speed at which it works. The removal or reduction of tarnish or corrosion products on metal objects may require relatively interventive cleaning treatments since they can be harder or more resistant than the bare metal. Therefore a compromise may be necessary in order to remove or reduce the corrosion products and not over clean the bare metal. The use of corrosion inhibitors in the cleaning treatment may be also be necessary to protect the exposed metal surfaces during treatment. However the efficiency and speed of a cleaning treatment may be one of the reasons why relatively aggressive interventive cleaning treatments are employed, as there may not be resources available in terms of time or staff to clean large numbers of metal objects with techniques that are relatively time consuming, such

as some of the more controlled abrasive cleaning techniques, for example precipitated calcium carbonate in a paste with ethanol. In addition, the use of abrasive treatments such as this are also not always recommended in the conservation of plated metal surfaces, as they can wear away the plating material exposing the base metal.

Health and safety considerations are another factor in the decisions making process for cleaning treatments. The choice of the materials and techniques can be dictated by the health and safety regulations in place, for example good ventilation and air extraction are required for the use of most chemicals, as well as solvents other than water in conservation. Cleaning treatments involving toxic and highly acidic or alkaline chemicals or long exposure times to chemicals that are toxic with prolonged exposure may not be possible if there is inadequate air extraction available, such as fume cupboards, ceiling fume extractors or portable air extraction units and personal protective equipment (PPE). The trend towards the use of less toxic chemicals in conservation in recent years is also a factor in the decision making process for cleaning treatments, as there has been an increasing awareness of the negative effects of exposure to chemicals used in conservation and stricter health and safety workplace regulations involving risk assessments for the different types of treatments carried out.

4.8 Future Research

The analysis of other conservation preparations or procedures and proprietary products, as well as other types of metals and tarnished or corroded metal surfaces could be carried out to add to the visual database or atlas of the effects of cleaning treatments for reference in metals conservation. For example the use of talc in a paste with ethanol for cleaning silver could be analysed by ESEM-EDX, following the same procedure to compare with the results for precipitated calcium carbonate in a paste with ethanol, as the hardness of talc (1) is less than that of calcium carbonate (3) as well silver/silver alloys (2.5-4) (Ted Pella Inc, 2013), and it should cause less scratching of the silver surface. Likewise in the conservation of copper, milder abrasive materials with a hardness less than that of copper (2.5-3) (Ted Pella Inc, 2013) could be analysed. The effects of proprietary products containing ammonia that are still recommended for the conservation of historic copper and iron objects, such as Autosol Metal Polish could also be analysed using the same procedure and the results added to the visual database.

Additional types of metals such as the copper alloys brass and bronze, as well as sterling silver and nickel silver could be tested to examine the visual effects of surface cleaning treatments

on alloys. The effects of surface cleaning treatments on modern metals such as aluminium and a range of modern plated metals could also be analysed. To complement the ESEM-EDX results for the range of bare metal surfaces analysed, further systematic analysis could be carried out on tarnished and corroded metal surfaces and the results compared. For example the effects of localised electrolytic reduction treatments for lead with corrosion could be analysed by ESEM-EDX as an alternative to chemical treatments such as EDTA, as this is recommended in the conservation literature for certain types of lead objects. Finally the question of residues from the surface cleaning treatments could be examined in greater detail through the use of analytical techniques that identify organic as well as inorganic materials, such as Raman spectroscopy and FTIR micro-spectroscopy.

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6.0 Appendices

6.1 Non-Invasive Characterisation of a Collection of Modern Religious Medals using Portable X-ray Fluorescence Spectroscopy

6.1.1 Digital photographs of the 60 modern religious medals

6.1.2 pXRF Results for the Metal Reference Standards

6.1.3 pXRF Results for the Internal Calibration of the Thermo Scientific Niton XL 3t pXRF analyzer

6.1.4 pXRF Results for the Reproducibility Tests - Medals 1-5

6.1.5 pXRF Results for Medals 1-60 – 1st and 2nd Sets of Data

6.1.6 ESEM-EDX Mapping Data for Medals with Plated and Corroded Surfaces

6.2 Analysing the Effects of Cleaning Treatments in Metals Conservation with Scanning Electron Microscopy - Energy Dispersive X-ray Spectroscopy

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6.2.2 ESEM-EDX Data for the Silver Coupons

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6.1 Non-Invasive Characterisation of a Collection of Modern Religious Medals using Portable X-ray Fluorescence Spectroscopy

6.1.1 Digital photographs of the 60 modern religious medals

Jesus Christ Medals: Scale 1:1

JC medal 1 - side 1

JC medal 1 - side 2

JC medal 2 - side 1

JC medal 2 - side 2

JC medal 3 – side 1

JC medal 3 – side 2

Jesus Christ Medals: Scale 1:1

JC medal 4 – side 1

JC medal 4 – side 2

JC medal 5 – side 1

JC medal 5 – side 2

JC medal 6 – side 1

JC medal 6 – side 2

JC medal 7 – side 1

JC medal 7 – side 2

Jesus Christ Medals: Scale 1:1

JC medal 8 - side 1

JC medal 8 - side 2

JC medal 9 – side 1

JC medal 9 – side 2

JC medal 10 – side 1

JC medal 10 – side 2

JC medal 11 – side 1

JC medal 11 – side 2

Jesus Christ Medals: Scale 1:1

JC medal 12 – side 1

JC medal 12 – side 2

JC medal 13 – side 1

JC medal 13 – side 2

JC medal 14 – side 1

JC medal 14 – side 2

JC medal 15 – side 1

JC medal 15 – side 2

Jesus Christ Medals: Scale 1:1

JC medal 16 – side 1

JC medal 16 – side 2

JC medal 17 – side 1

JC medal 17 – side 2

Infant of Prague Medals: Scale 1:1

IOP medal 18 – side 1

IOP medal 18 - side 2

IOP medal 19 – side 1

IOP medal 19 – side 2

Infant of Prague Medals: Scale 1:1

IOP medal 20 – side 1

IOP medal 20 – side 2

IOP medal 21 – side 1

IOP medal 21 – side 2

IOP medal 22 – side 1

IOP medal 22 – side 2

IOP medal 23 – side 1

IOP medal 23 – side 2

Madonna and Child Medals: Scale 1:1

MC medal 24 – side 1

MC medal 24 – side 2

MC medal 25 – side 1

MC medal 25 – side 2

MC medal 26 – side 1

MC medal 26 – side 2

MC medal 27 – side 1

MC medal 27 – side 2

Madonna and Child Medals: Scale 1:1

MC medal 28 – side 1

MC medal 28 – side 2

MC medal 29 – side 1

MC medal 29 – side 2

MC medal 30 – side 1

MC medal 30 – side 2

MC medal 31 – side 1

MC medal 31 – side 2

Madonna and Child Medals: Scale 1:1

MC medal 32 – side 1

MC medal 32 – side 2

MC medal 33 – side 1

MC medal 33 – side 2

Blessed Sacrament Medals: Scale 1:1

BS medal 34 – side 1

BS medal 34 – side 2

Blessed Sacrament Medals: Scale 1:1

BS medal 35 – side 1

BS medal 35 – side 2

BS medal 36 – side 1

BS medal 36 – side 2

BS medal 37 – side 1

BS medal 37 – side 2

Blessed Sacrament Medals: Scale 1:1

BS medal 38 – side 1

BS medal 38 – side 2

BS medal 39 – side 1

BS medal 39 – side 2

Madonna and Child Medals: Scale 1:1

MC medal 40 – side 1

MC medal 40 – side 2

Madonna and Child Medals: Scale 1:1

MC medal 41 – side 1

MC medal 41 – side 2

MC medal 42 – side 1

MC medal 42 – side 2

MC medal 43 – side 1

MC medal 43 – side 2

Madonna and Child Medals: Scale 1:1

MC medal 44 – side 1

MC medal 44 – side 2

MC medal 45 – side 1

MC medal 45 – side 2

MC medal 46 – side 1

MC medal 46 – side 2

MC medal 47 – side 1

MC medal 47 – side 2

Madonna and Child Medals: Scale 1:1

MC medal 48 – side 1

MC medal 48- side 2

MC medal 49 – side 1

MC medal 49 – side 2

MC medal 50 – side 1

MC medal 50 – side 2

Diverse Medals: Scale 1:1

D medal 51 –side 1

D medal 51 – side 2

D medal 52 – side 1

D medal 52 – side 2

D medal 53 – side 1

D medal 53 – side 2

Diverse Medals: Scale 1:1

D medal 54 – side 1

D medal 54 – side 2

D medal 55 – side 1

D medal 55 – side 2

D medal 56 – side 1

D medal 56 – side 1

D medal 57 – side 1

D medal 57 – side 2

Diverse Medals: Scale 1:1

D medal 58 – side 1

D medal 58 – side 2

D medal 59 – side 1

D medal 59 – side 2

D medal 60 – side 1

D medal 60 – side 2

6.1.2 pXRF Results for the Metal Reference Standards

6.1.3 pXRF Results for the Internal Calibration of the Thermo Scientific Niton XL 3t pXRF analyzer

6.1.4 pXRF Results for the Reproducibility Tests - Medals 1-5

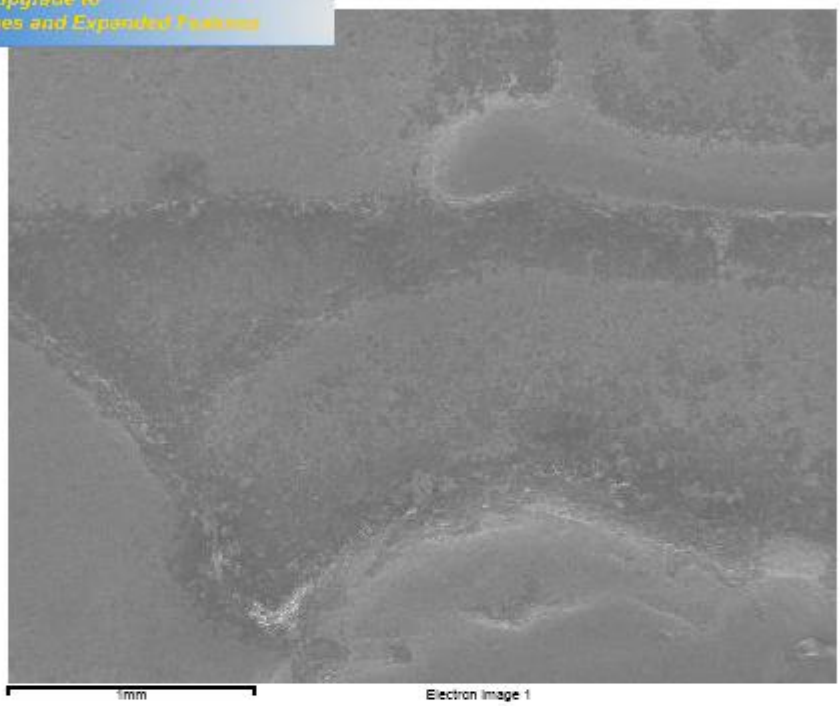
6.1.5 pXRF Results for Medals 1-60 – 1st and 2nd Sets of Data

6.1.6 ESEM-EDX Mapping Data for Medals with Plated and Corroded Surfaces

N.B.: The print outs of some of the ESEM-EDX mapping images are not as clear as the original images.

ESEM-EDX Results for Medal 2 side 2: area above Christ's head at 80x

8/25/2011 3:27:55 PM



Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 2

Standard :
O SiO2 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
S FeS2 1-Jun-1999 12:00 AM
Cu Cu 1-Jun-1999 12:00 AM
Ag Ag 1-Jun-1999 12:00 AM

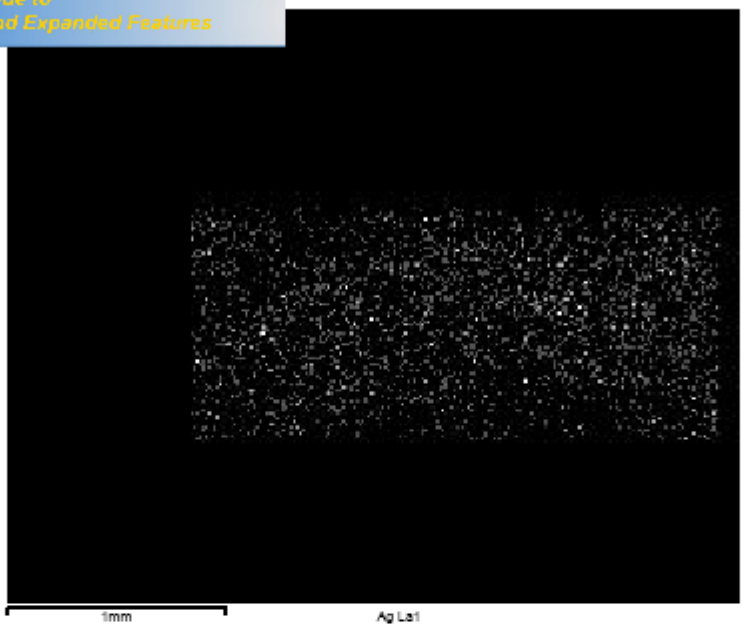
Element	Weight%	Atomic%
O K	16.78	50.01
Si K	4.73	8.03
S K	4.74	7.05
Cu K	7.52	5.64
Ag L	66.23	29.27
Totals	100.00	

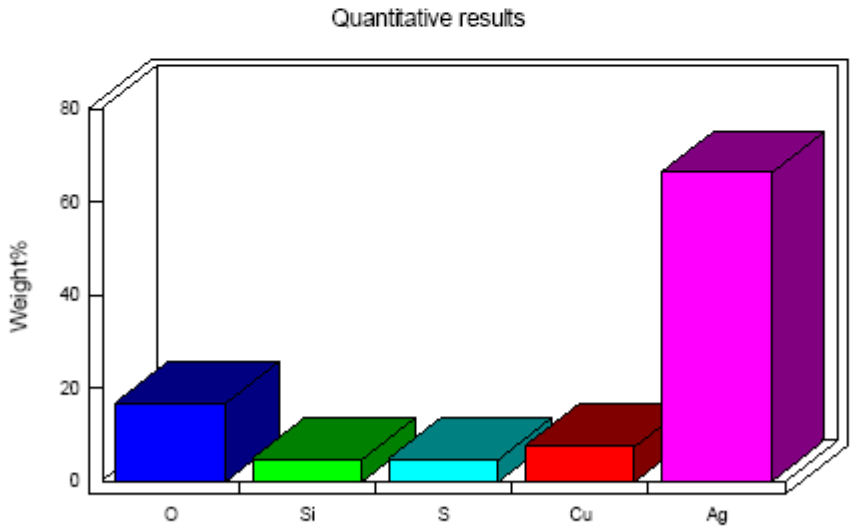
Comment:

INCA

ESEM-EDX Results for Medal 2 side 2: silver (Ag) mapping - area above Christ's head at 80x

8/25/2011 3:30:29 PM



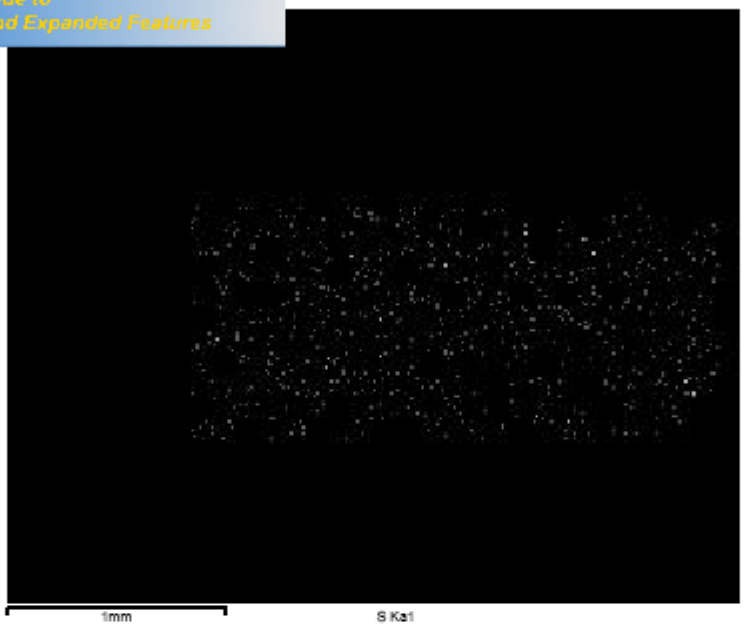


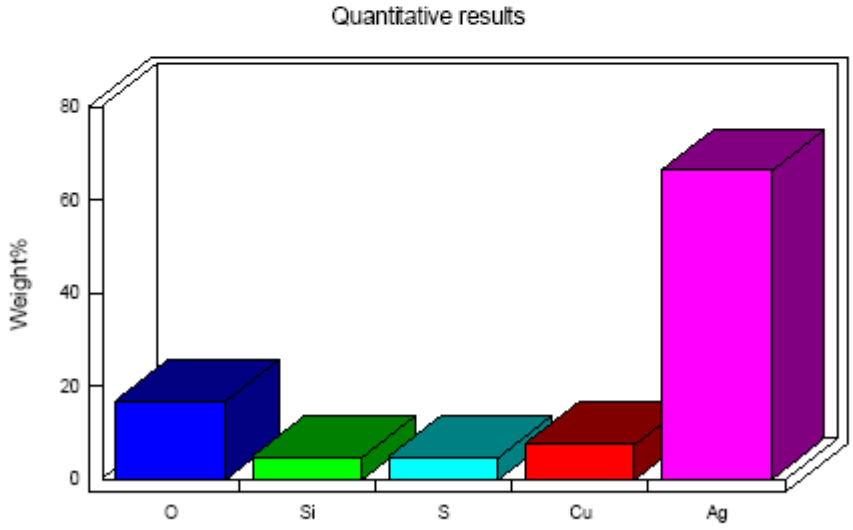
Comment: Medal 2 side 2 - area above J.C.'s head 80 x

INCA

ESEM-EDX Results for Medal 2 side 2: sulphur (S) mapping - area above Christ's head at 80x

8/25/2011 3:31:01 PM





Comment: Medal 2 side 2 - area above J.C.'s head 80 x

INCA

ESEM-EDX Results for Medal 10 side 2: central area proper right side at 40x

8/19/2011 6:10:05 PM

Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 2

Standard :
C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
S FeS2 1-Jun-1999 12:00 AM
Cu Cu 1-Jun-1999 12:00 AM
Ag Ag 1-Jun-1999 12:00 AM

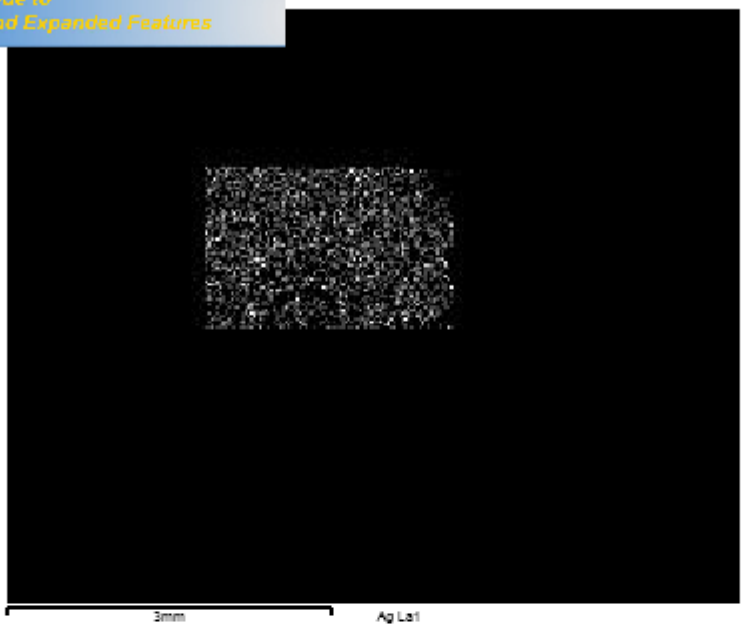
Element	Weight%	Atomic%
C K	14.41	30.05
O K	35.78	56.04
S K	2.56	2.00
Cu L	5.72	2.26
Ag L	41.52	9.65
Totals	100.00	

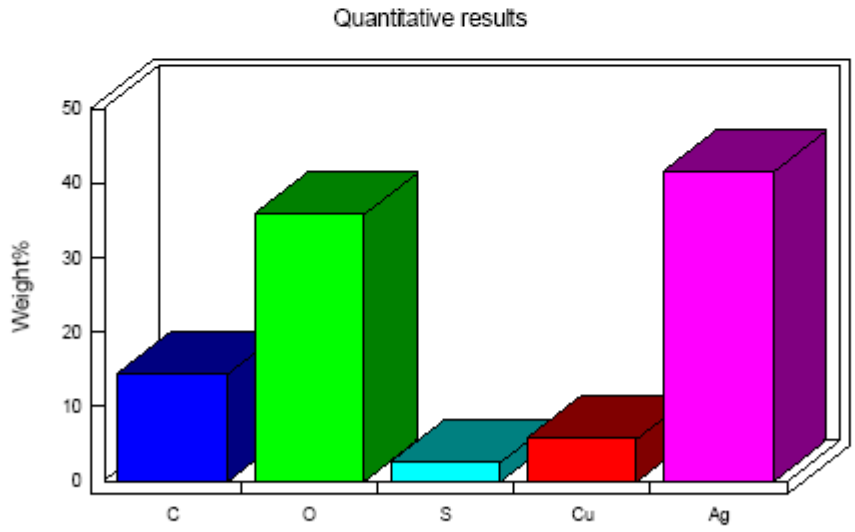
Comment: Medal 10 side 2 - central area 40 x

INCA

ESEM-EDX Results for Medal 10 side 2: silver (Ag) mapping - central area proper right side at 40x

8/19/2011 6:09:16 PM



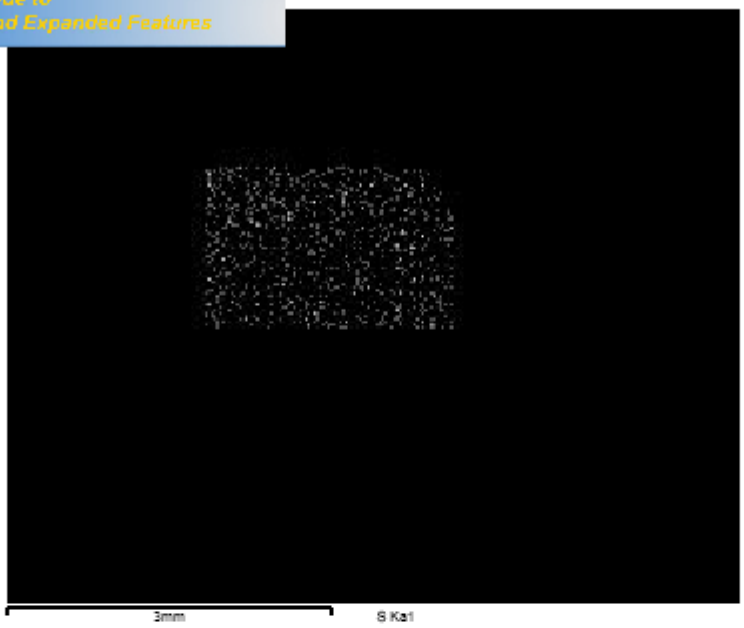


Comment: Medal 10 side 2 - central area 40 x

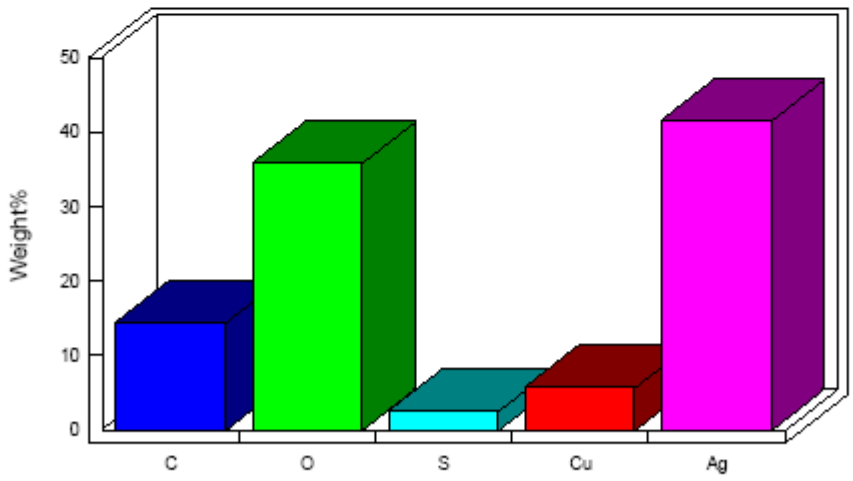
inca

ESEM-EDX Results for Medal 10 side 2: sulphur (S) mapping - central area proper right side at 40x

8/19/2011 6:11:14 PM



Quantitative results



Comment: Medal 10 side 2 - central area 40 x

inca

ESEM-EDX Results for Medal 13 side 1: central area with the heart at 40x

.2011 8/26/2011 6:35:54 PM

Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 1

Standard :
Ni Ni 1-Jun-1999 12:00 AM
Cu Cu 1-Jun-1999 12:00 AM
Zn Zn 1-Jun-1999 12:00 AM
Ag Ag 1-Jun-1999 12:00 AM

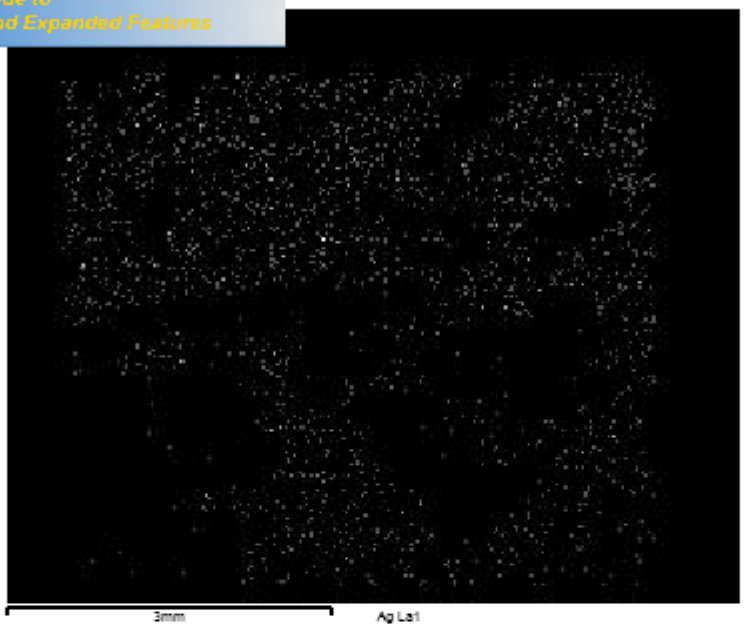
Element	Weight%	Atomic%
Ni K	5.95	8.70
Cu K	21.91	29.62
Zn K	8.18	10.75
Ag L	63.96	50.93
Totals	100.00	

Comment: Medal 13 side 1 - area with heart motif 40 x

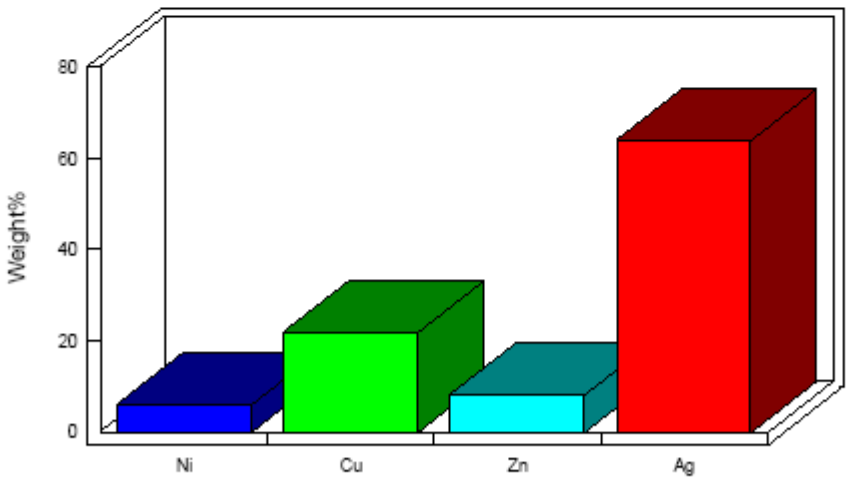
INCA

ESEM-EDX Results for Medal 13 side 1: silver (Ag) mapping - central area with the heart at 40x

.2011 8/26/2011 6:38:42 PM



Quantitative results

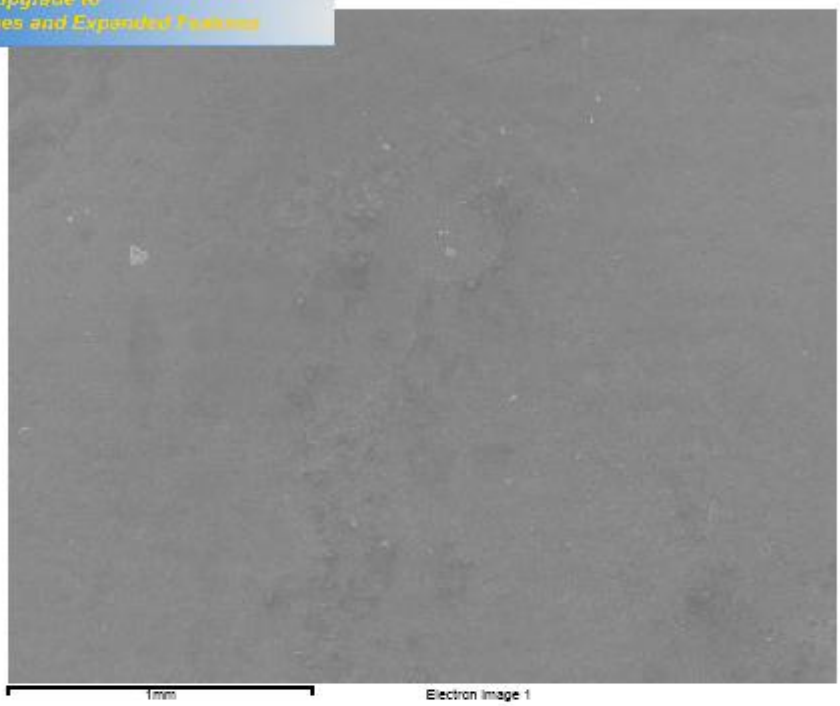


Comment: Medal 13 side 1 - area with heart motif 40 x

inca

ESEM-EDX Results for Medal 16 side 1: front of neck area at 100x

8/25/2011 5:16:52 PM



Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 2

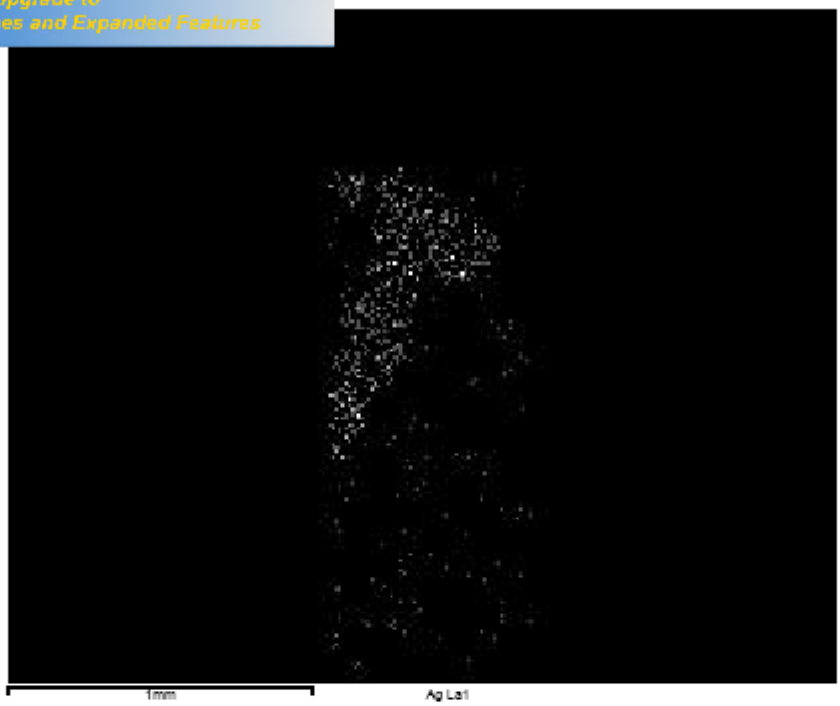
Standard :
O SiO2 1-Jun-1999 12:00 AM
Cl KCl 1-Jun-1999 12:00 AM
Ni Ni 1-Jun-1999 12:00 AM
Cu Cu 1-Jun-1999 12:00 AM
Zn Zn 1-Jun-1999 12:00 AM
Ag Ag 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	27.58	61.64
Cl K	1.76	1.78
Ni K	5.86	3.57
Cu K	35.33	19.88
Zn K	15.56	8.51
Ag L	13.90	4.61
Totals	100.00	

Comment: Medal 16 side 1 - neck area 100x

ESEM-EDX Results for Medal 16 side 1: silver (Ag) mapping – front of neck area at 100x

8/25/2011 5:18:25 PM



Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 2

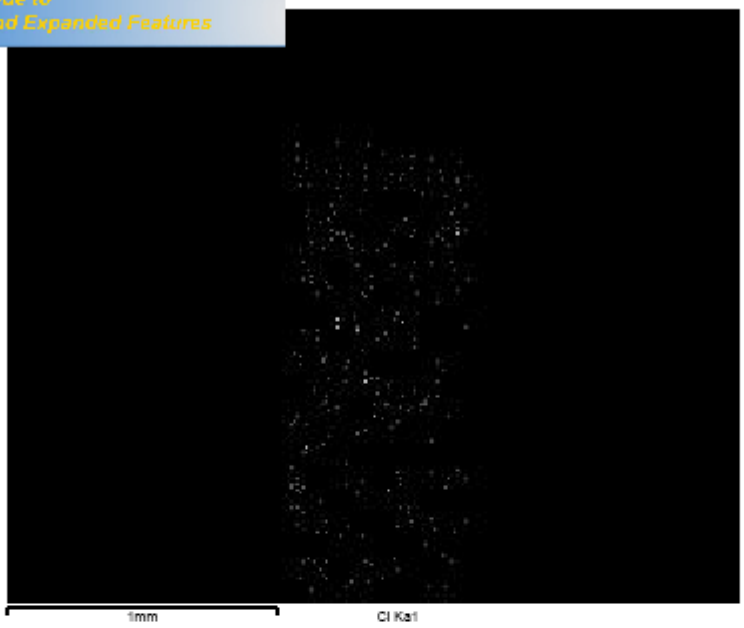
Standard :
O SiO2 1-Jun-1999 12:00 AM
Cl KCl 1-Jun-1999 12:00 AM
Ni Ni 1-Jun-1999 12:00 AM
Cu Cu 1-Jun-1999 12:00 AM
Zn Zn 1-Jun-1999 12:00 AM
Ag Ag 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	27.58	61.64
Cl K	1.76	1.78
Ni K	5.86	3.57
Cu K	35.33	19.88
Zn K	15.56	8.51
Ag L	13.90	4.61
Totals	100.00	

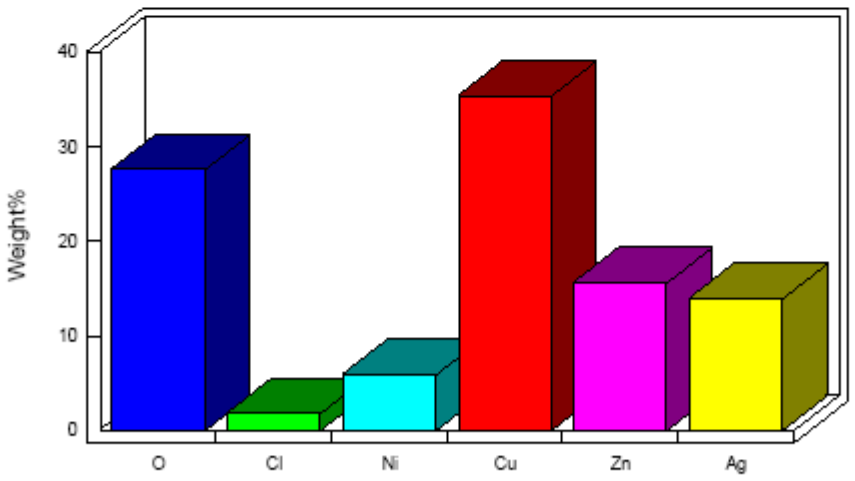
Comment: Medal 16 side 1 - neck area 100x

ESEM-EDX Results for Medal 16 side 1: chlorine (Cl) mapping – front of neck area at 100x

8/25/2011 5:20:08 PM



Quantitative results

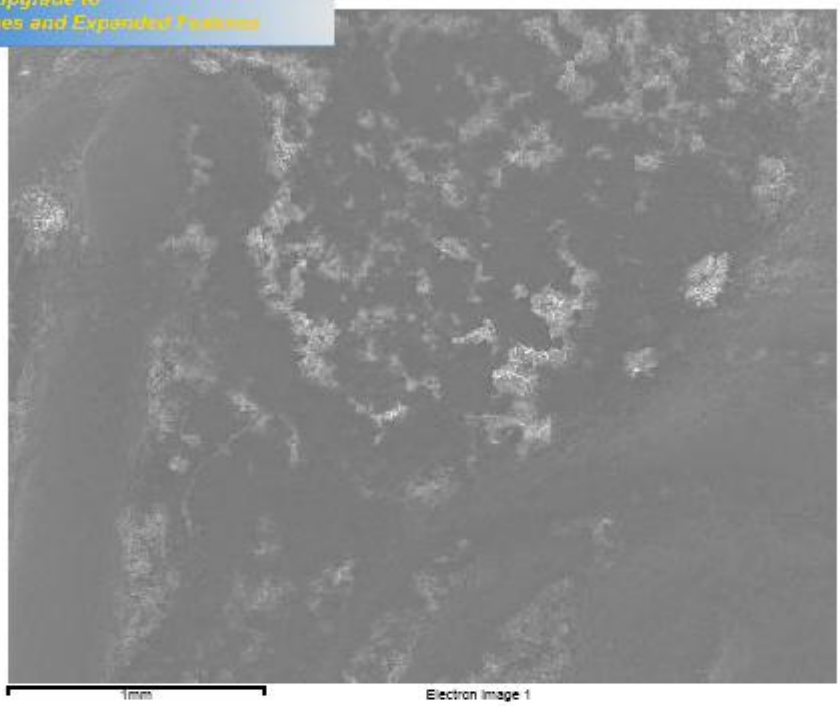


Comment: Medal 16 side 1 - neck area 100x

INCA

ESEM-EDX Results for Medal 26 side 1: area of green corrosion adjacent to the proper right side of the Madonna's head at 83x

8/25/2011 11:31:19 AM



Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 2

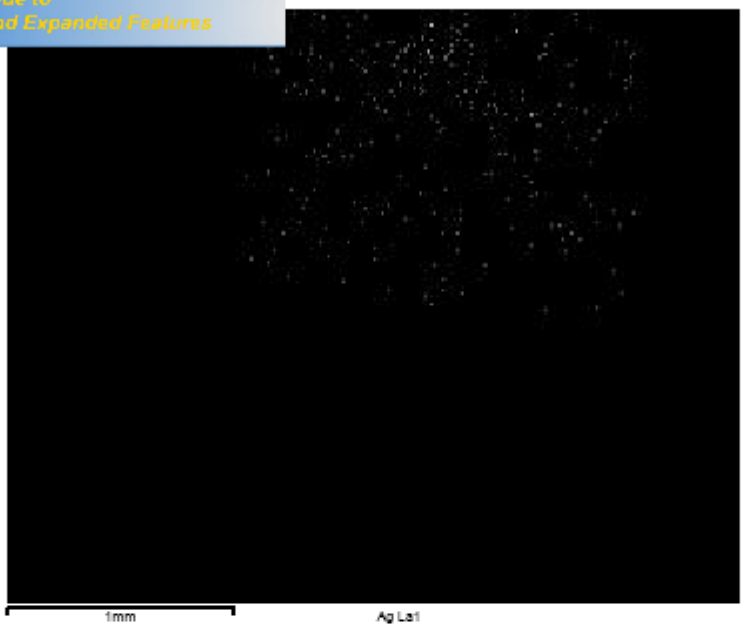
Standard :
O SiO2 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
S FeS2 1-Jun-1999 12:00 AM
Cl KCl 1-Jun-1999 12:00 AM
Ca Wollastonite 1-Jun-1999 12:00 AM
Cu Cu 1-Jun-1999 12:00 AM
Ag Ag 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	49.06	75.78
Si K	2.07	1.82
S K	3.99	3.08
Cl K	7.05	4.91
Ca K	1.01	0.63
Cu K	33.44	13.01
Ag L	3.38	0.78

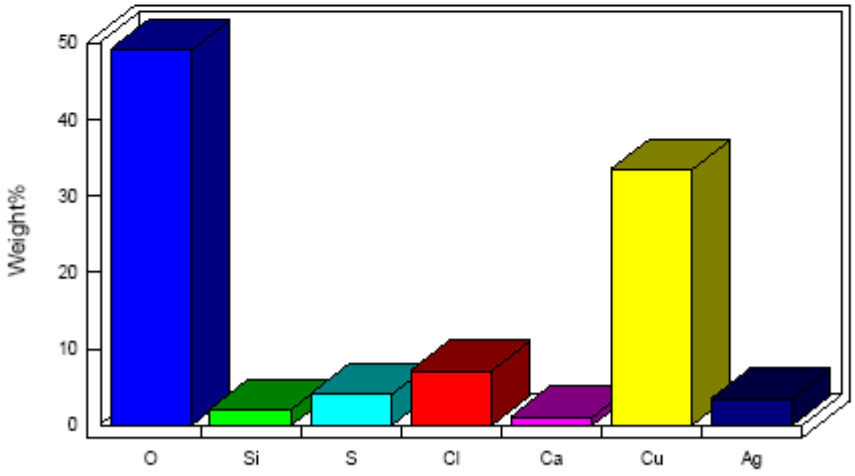
Comment: Medal 26 side 1 - area of green corrosion adjacent to P.R. side of M's head 83 x

ESEM-EDX Results for Medal 26 side 1: silver (Ag) mapping - area of green corrosion adjacent to the proper right side of the Madonna's head at 83x

8/25/2011 11:32:18 AM



Quantitative results

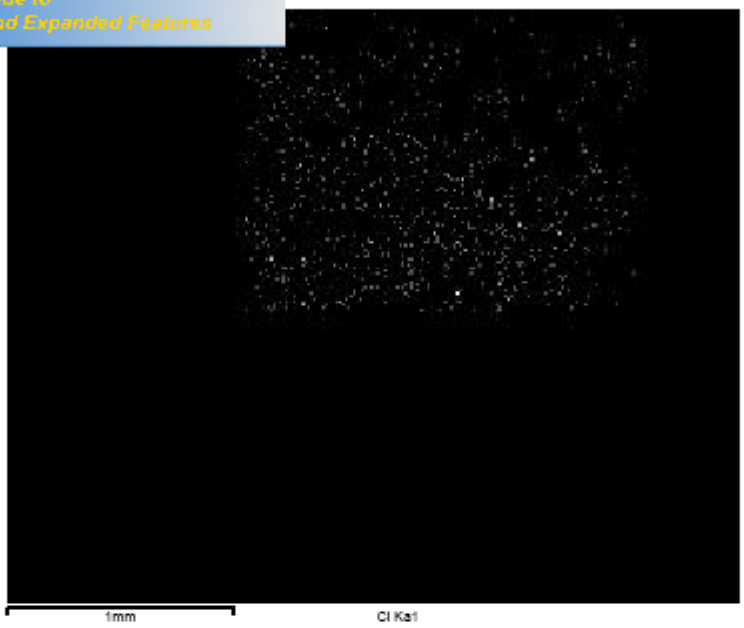


Comment: Medal 26 side 1 - area of green corrosion adjacent to P.R. side of M's head 83 x

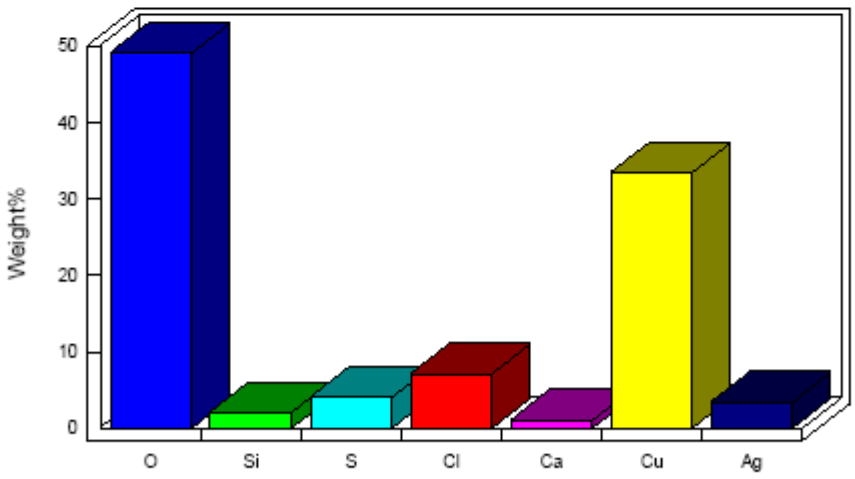
INCA

ESEM-EDX Results for Medal 26 side 1: chlorine (Cl) mapping - area of green corrosion adjacent to the proper right side of Madonna's head at 83x

8/25/2011 11:33:20 AM



Quantitative results

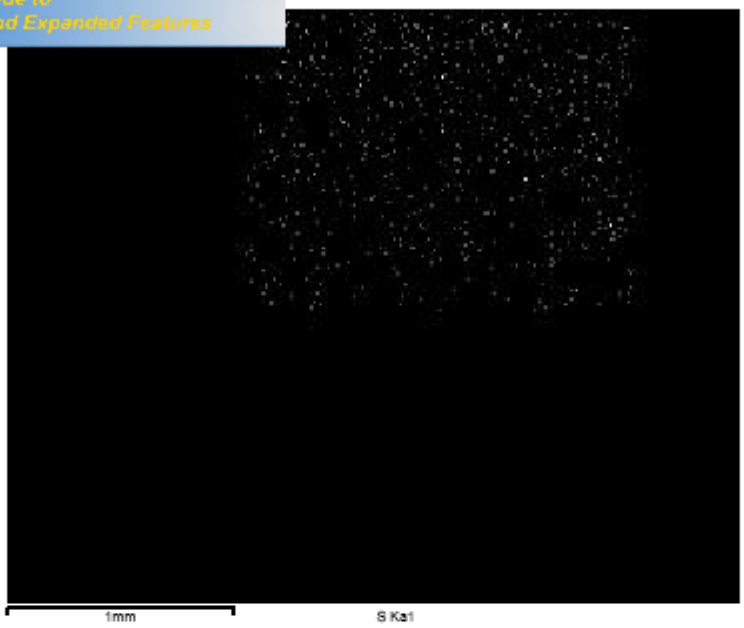


Comment: Medal 26 side 1 - area of green corrosion adjacent to P.R. side of M's head 83 x

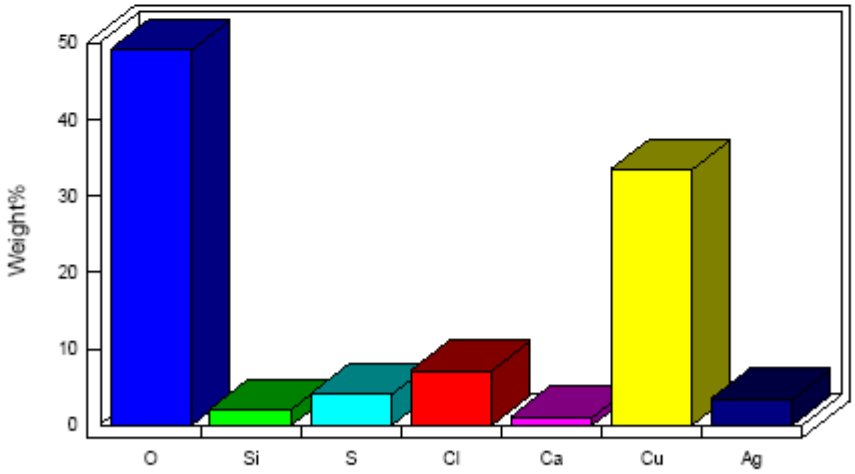
INCA

ESEM-EDX Results for Medal 26 side 1: sulphur (S) mapping - area of green corrosion adjacent to the proper right side of Madonna's head at 83x

8/25/2011 11:33:40 AM



Quantitative results

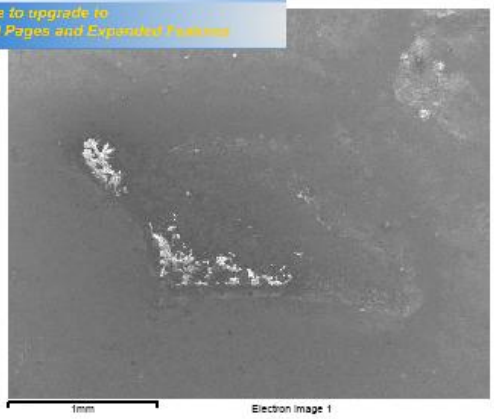


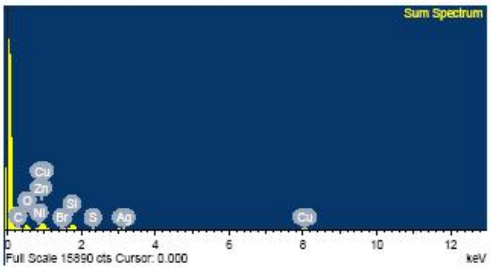
Comment: Medal 26 side 1 - area of green corrosion adjacent to P.R. side of M's head 83 x

INCA

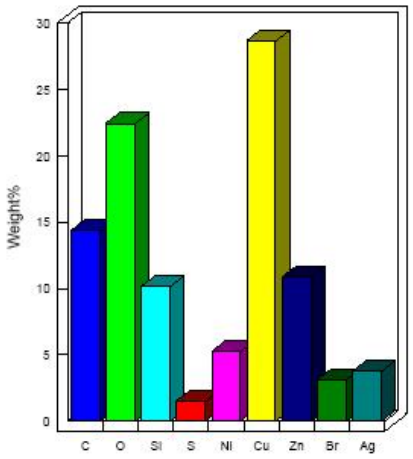
ESEM-EDX Results for Medal 27 side 1: area under Madonna's proper left arm at 84x

8/19/2011 4:21:04 PM





Quantitative results

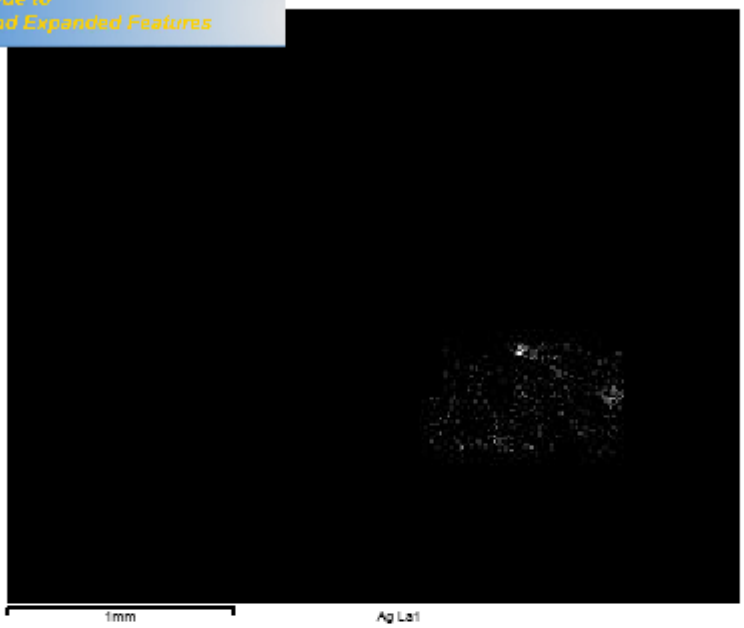


Comment: Medal 27 side 1 - area under PL arm of M - 84 x

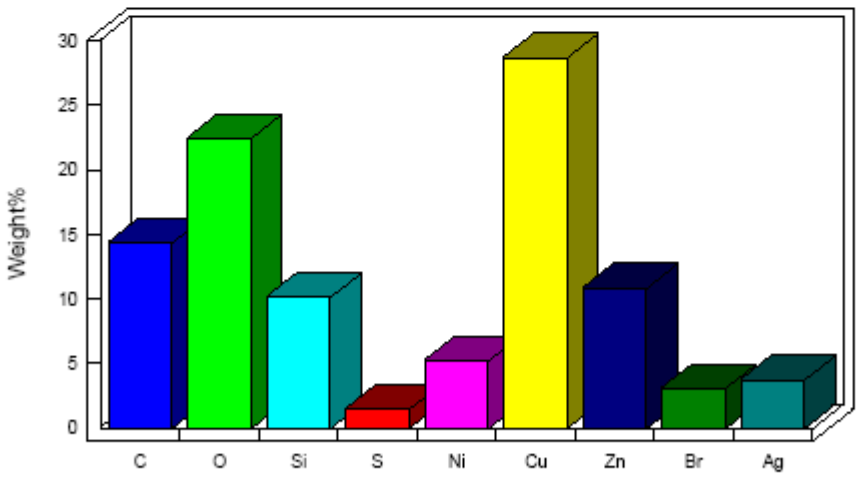
inca

ESEM-EDX Results for Medal 27 side 1: silver (Ag) mapping - area under Madonna's proper left arm at 84x

8/19/2011 4:22:13 PM



Quantitative results

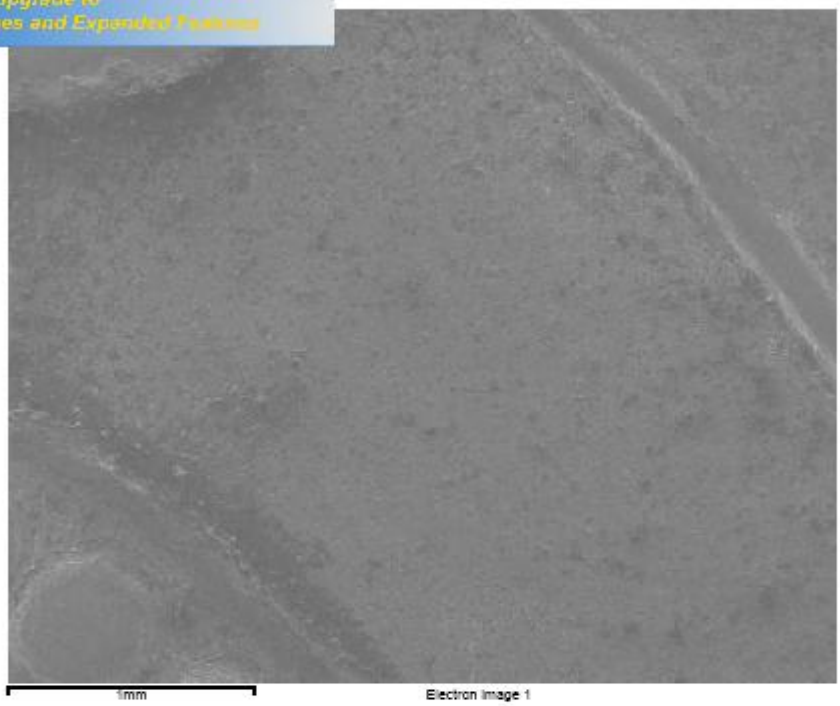


Comment: Medal 27 side 1 - area under PL arm of M - 84 x

INCA

ESEM-EDX Results for Medal 38 side 1: upper background area proper left side at 80x

8/25/2011 4:03:36 PM



Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 2

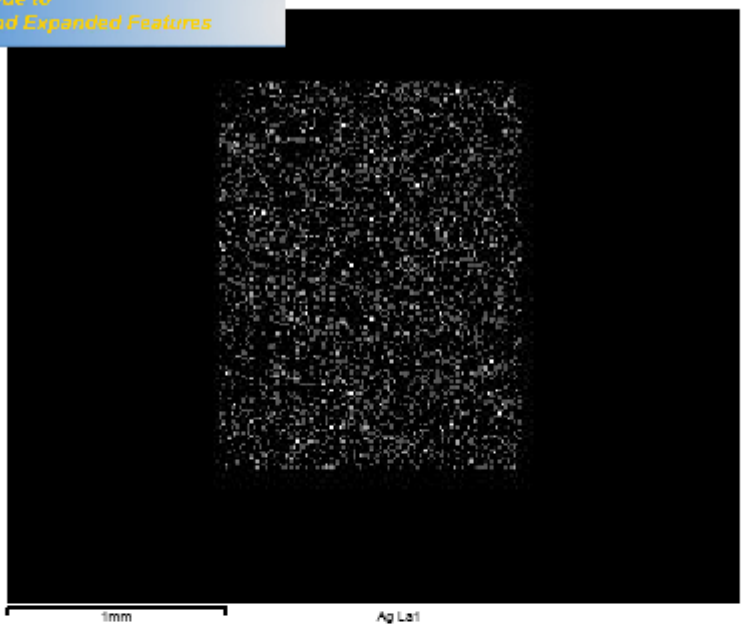
Standard :
C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
S FeS2 1-Jun-1999 12:00 AM
Cl KCl 1-Jun-1999 12:00 AM
Cu Cu 1-Jun-1999 12:00 AM
Ag Ag 1-Jun-1999 12:00 AM

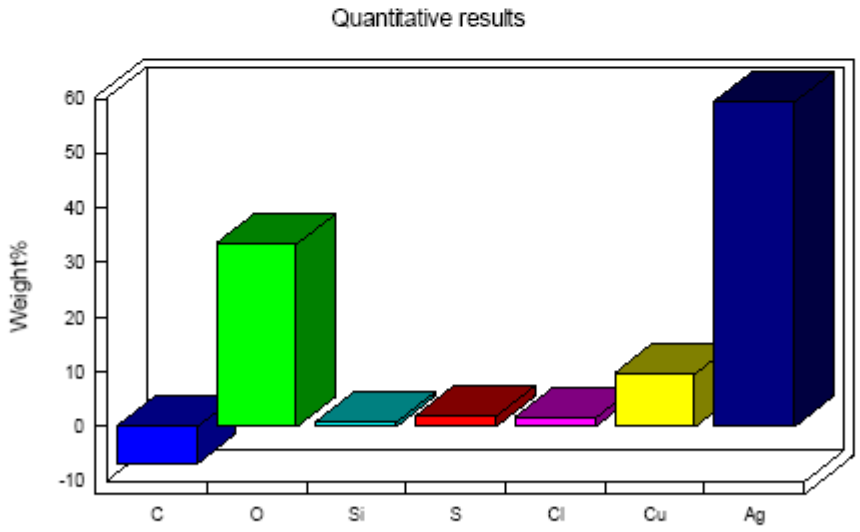
Element	Weight%	Atomic%
C K	-6.77	-23.88
O K	33.43	88.52
Si K	0.79	1.20
S K	1.89	2.49
Cl K	1.58	1.89
Cu K	9.67	6.45
Ag L	59.41	23.33

Comment: Medal 38 side 1 - background area upper P.L. side 80 x

ESEM-EDX Results for Medal 38 side 1: silver (Ag) mapping - upper background area proper left side at 80x

8/25/2011 4:04:18 PM



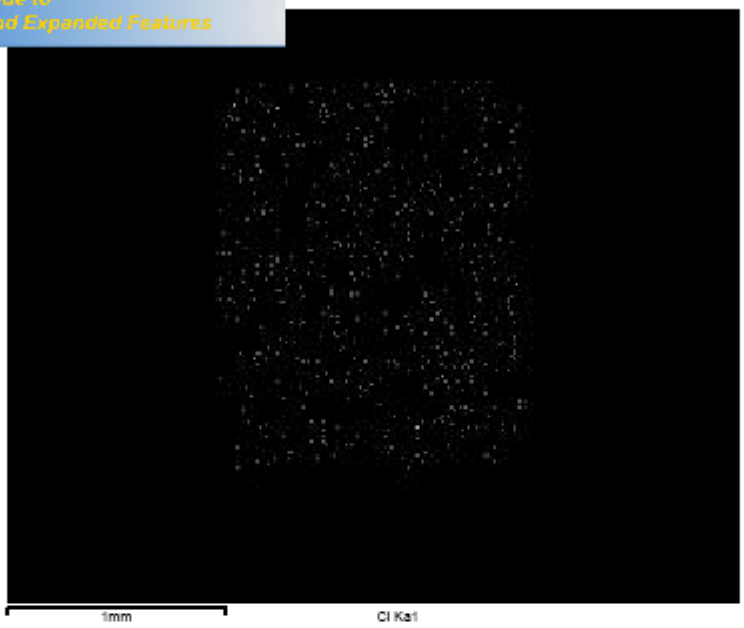


Comment: Medal 38 side 1 - background area upper P.L. side 80 x

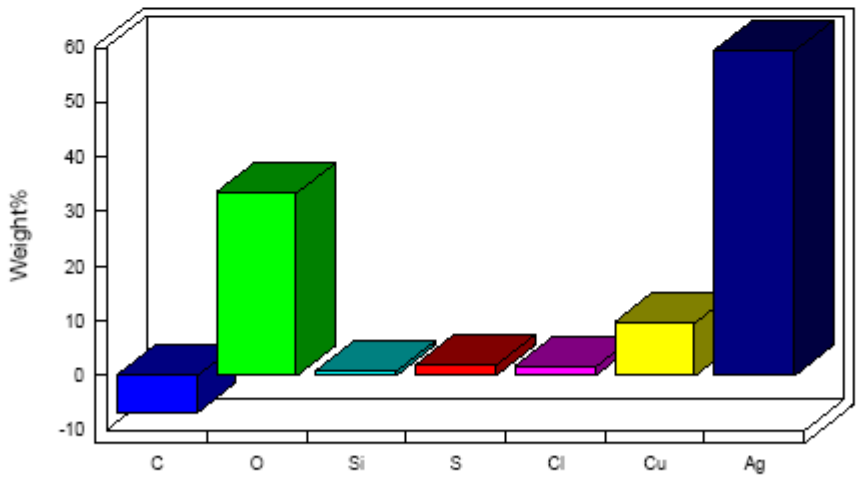
INCA

ESEM-EDX Results for Medal 38 side 1: chlorine (Cl) mapping – upper background area proper left side at 80x

8/25/2011 4:05:51 PM



Quantitative results

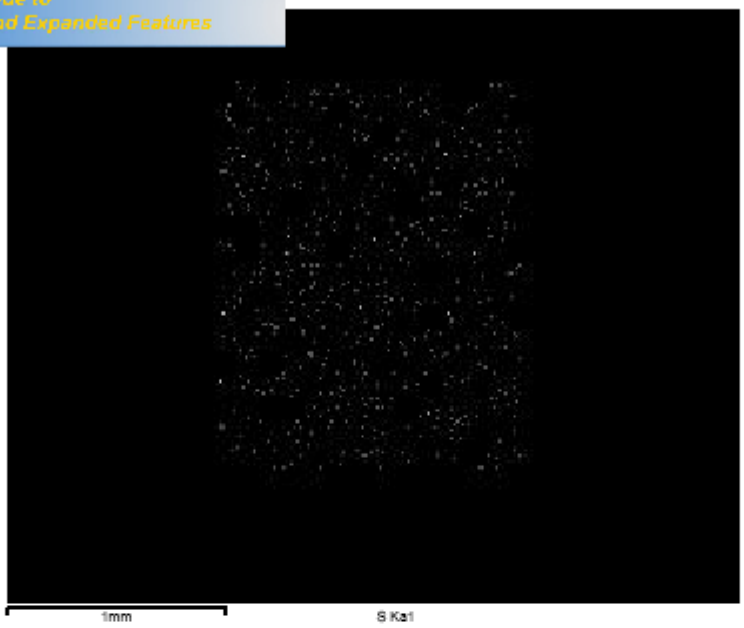


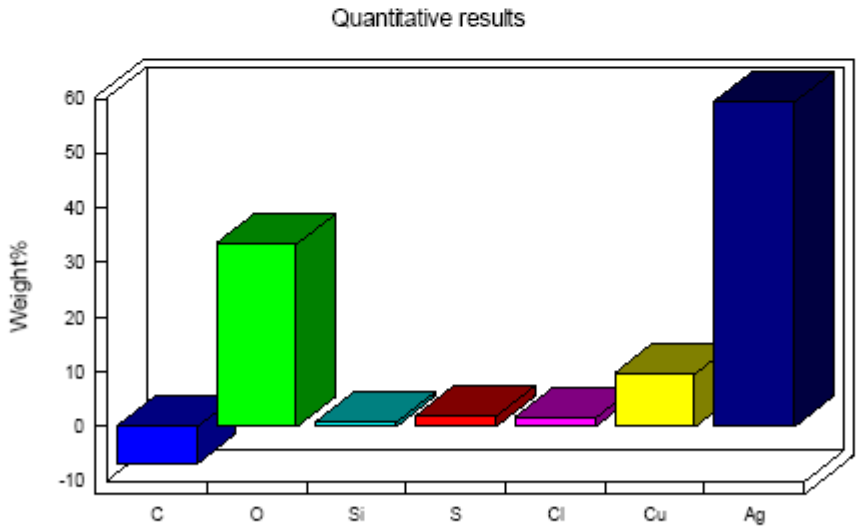
Comment: Medal 38 side 1 - background area upper P.L. side 80 x

inca

ESEM-EDX Results for Medal 38 side 1: sulphur (S) mapping – upper background area proper left side at 80x

8/25/2011 4:06:09 PM



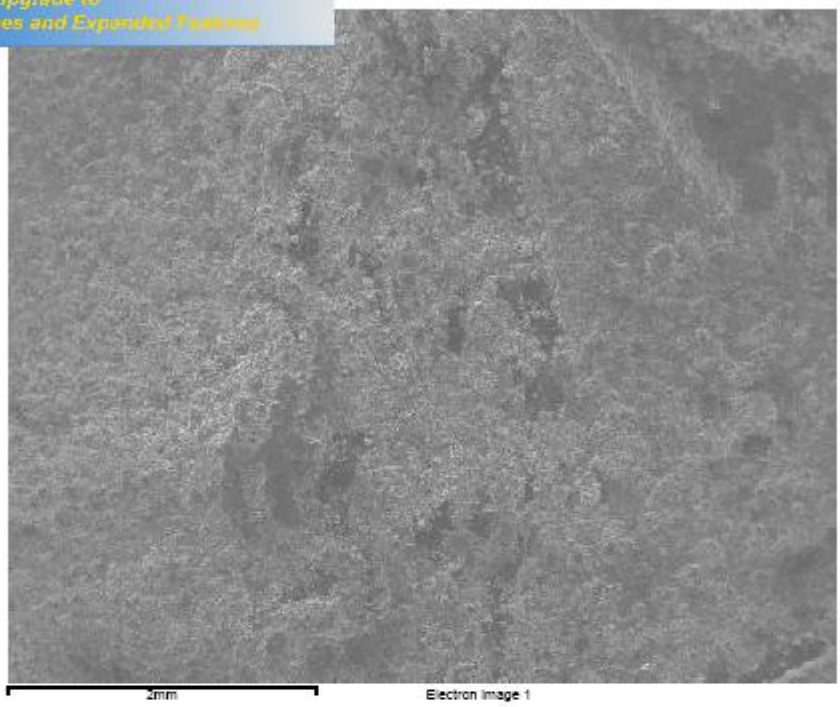


Comment: Medal 38 side 1 - background area upper P.L. side 80 x

inca

ESEM-EDX Results for Medal 41 side 2: light green deposit on proper right side of neck at 50x

8/25/2011 5:48:31 PM



Spectrum processing :
Peak possibly omitted : 5.640 keV

Processing option : All elements analyzed (Normalised)
Number of iterations = 1

Standard :
O SiO2 1-Jun-1999 12:00 AM
K MAD-10 Feldspar 1-Jun-1999 12:00 AM
Cu Cu 1-Jun-1999 12:00 AM
Zn Zn 1-Jun-1999 12:00 AM
Ag Ag 1-Jun-1999 12:00 AM

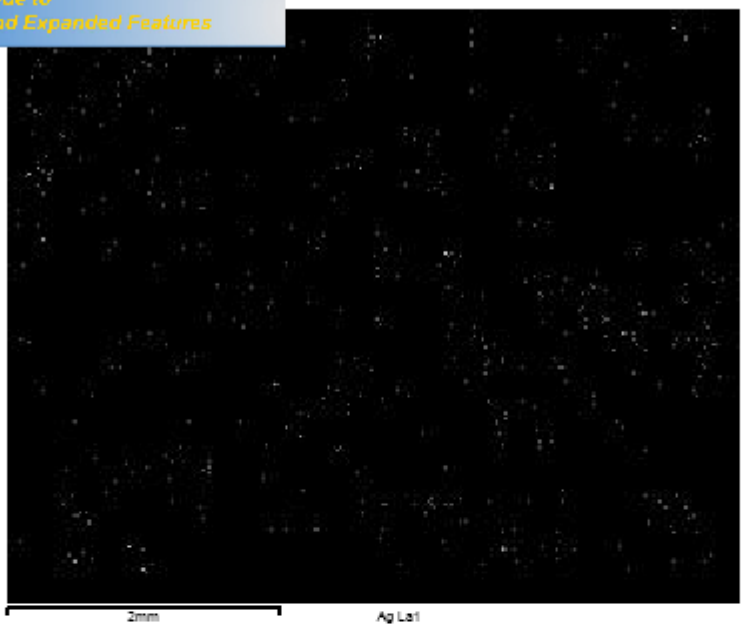
Element	Weight%	Atomic%
O K	23.41	56.33
K K	1.72	1.70
Cu K	24.54	14.87
Zn K	39.38	23.19
Ag L	10.95	3.91
Totals	100.00	

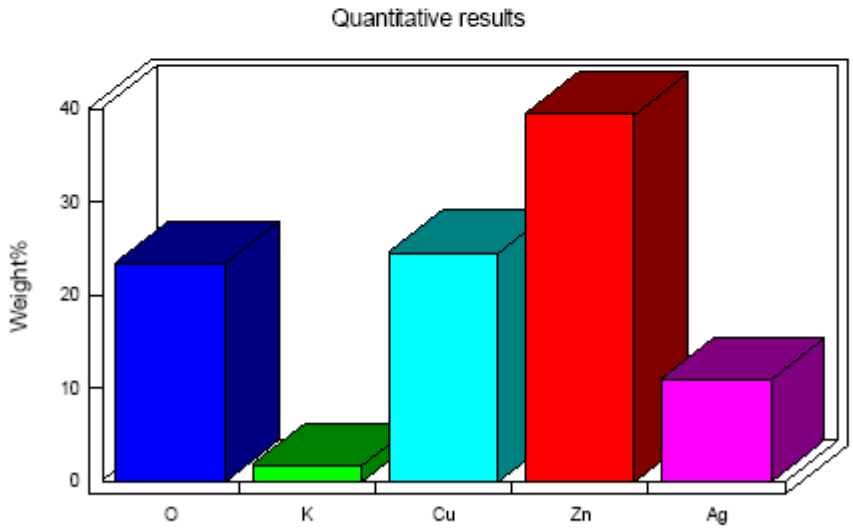
Comment: Medal 41 side 2 - light green deposit P.R. side of head 50 x

inca

ESEM-EDX Results for Medal 41 side 2: silver (Ag) mapping - light green deposit on proper right side of neck at 50x

8/25/2011 5:51:10 PM



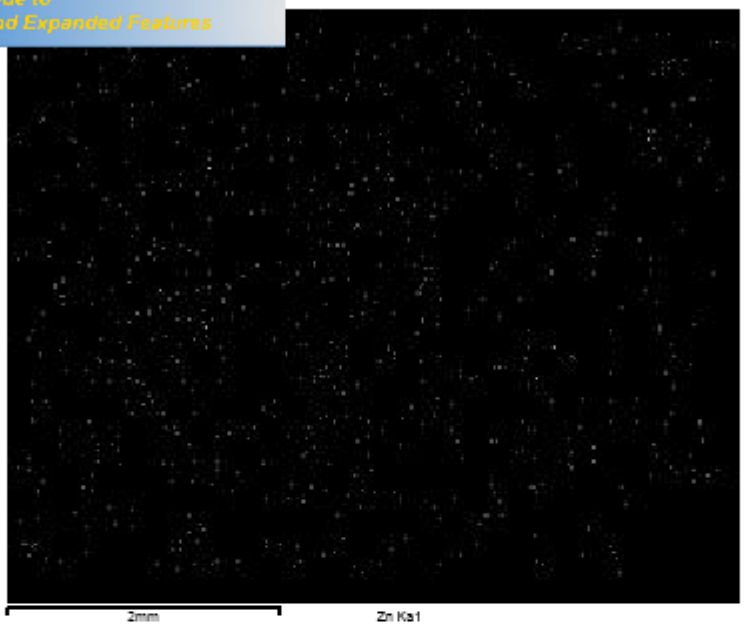


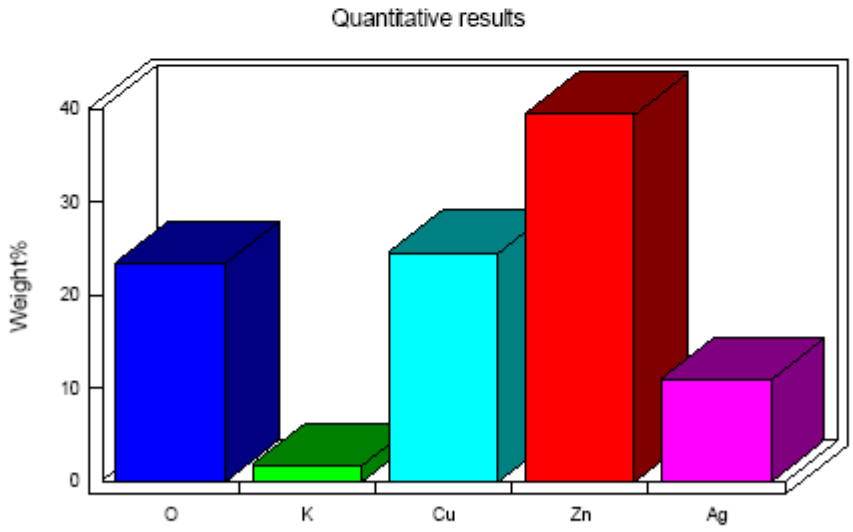
Comment: Medal 41 side 2 - light green deposit P.R. side of head 50 x

INCA

ESEM-EDX Results for Medal 41 side 2: zinc (Zn) mapping - light green deposit on proper right side of neck at 50x

8/25/2011 5:51:25 PM



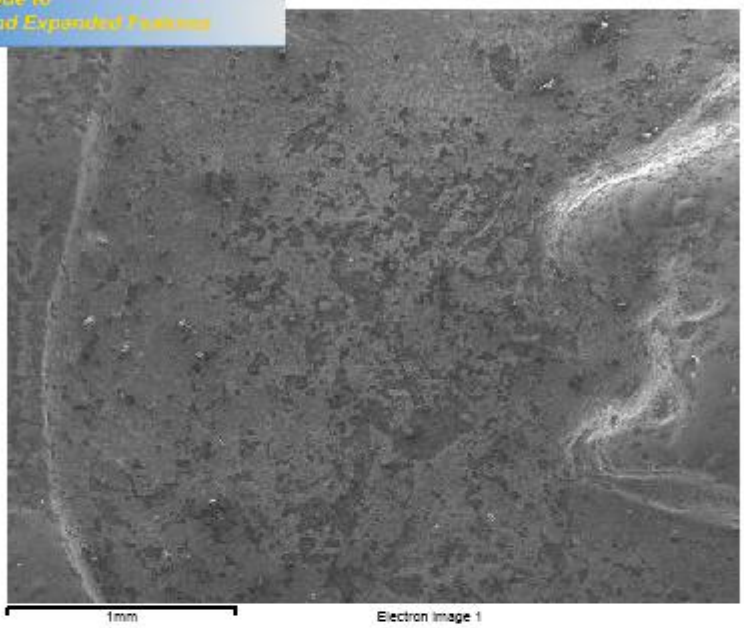


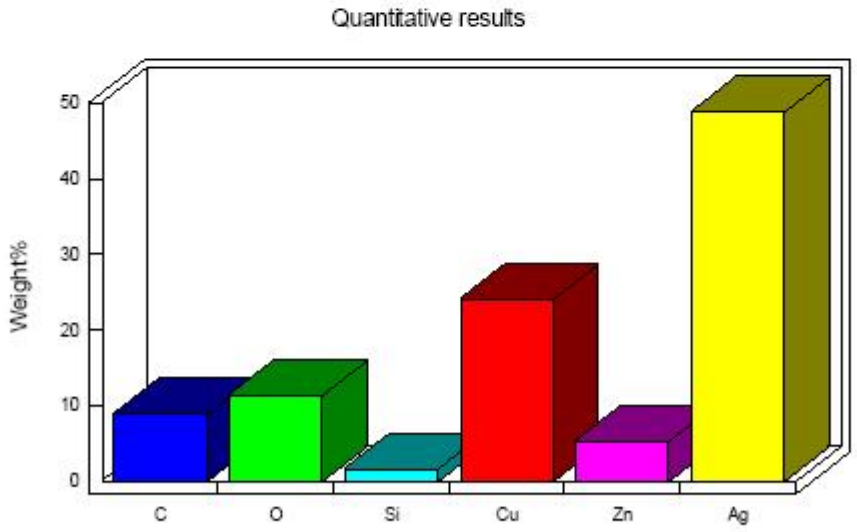
Comment: Medal 41 side 2 - light green deposit P.R. side of head 50 x

INCA

ESEM-EDX Results for Medal 42 side 2: neck area at 84x

11 8/19/2011 1:28:57 PM



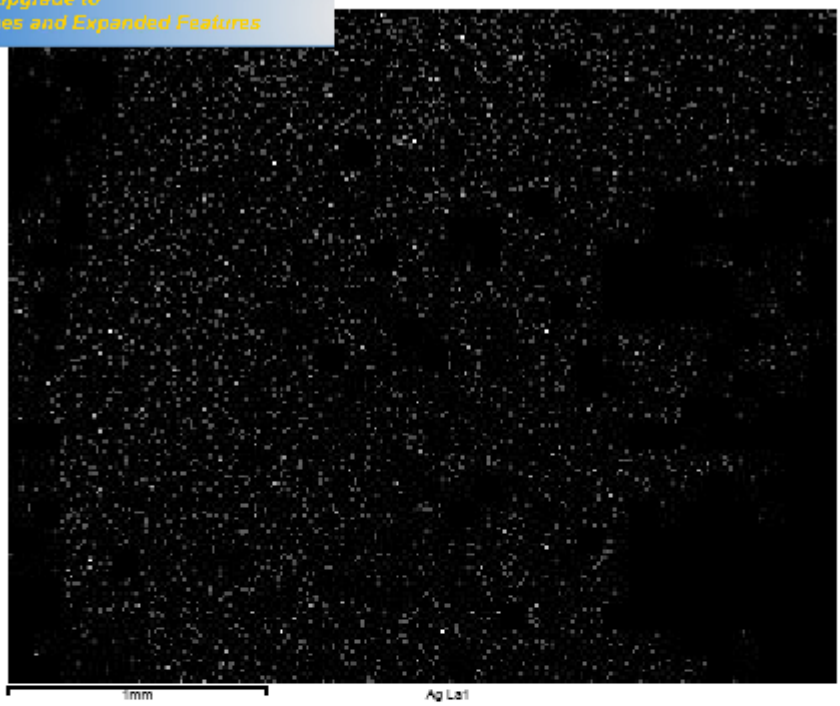


Comment: Medal 42 side 1 - neck are under beard 84 x

INCA

ESEM-EDX Results for Medal 42 side 2: silver (Ag) mapping – neck area at 84x

11 8/19/2011 1:31:21 PM



Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 2

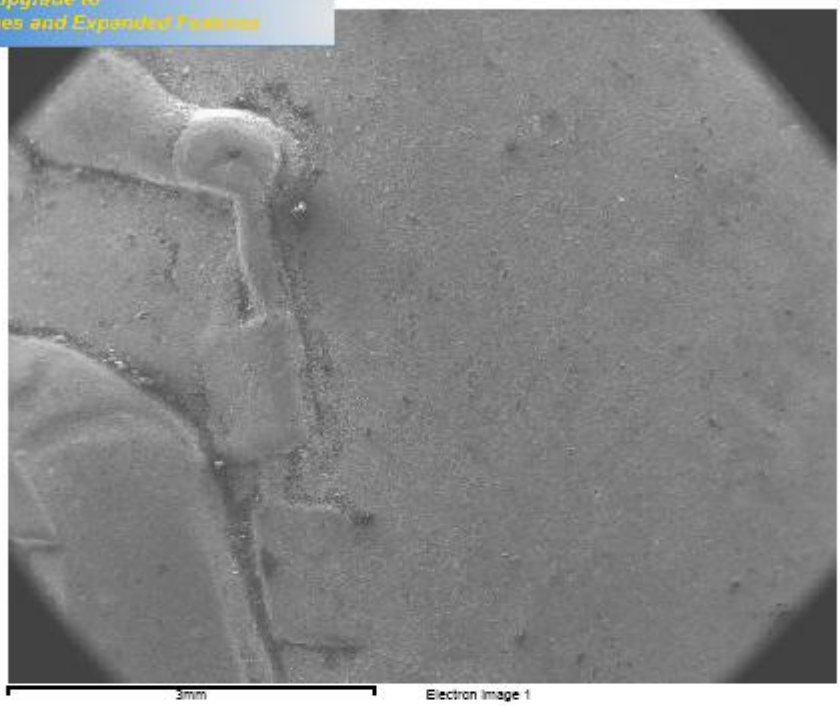
Standard :
C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
Cu Cu 1-Jun-1999 12:00 AM
Zn Zn 1-Jun-1999 12:00 AM
Ag Ag 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	8.85	30.51
O K	11.33	29.32
Si K	1.59	2.35
Cu L	24.07	15.69
Zn L	5.33	3.38
Ag L	48.83	18.75
Totals	100.00	

Comment: Medal 42 side 1 - neck are under beard 84 x

ESEM-EDX Results for Medal 43 side 1: background area proper left side at 40x

8/19/2011 3:02:22 PM



Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 2

Standard :
C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
S FeS2 1-Jun-1999 12:00 AM
Cu Cu 1-Jun-1999 12:00 AM
Ag Ag 1-Jun-1999 12:00 AM

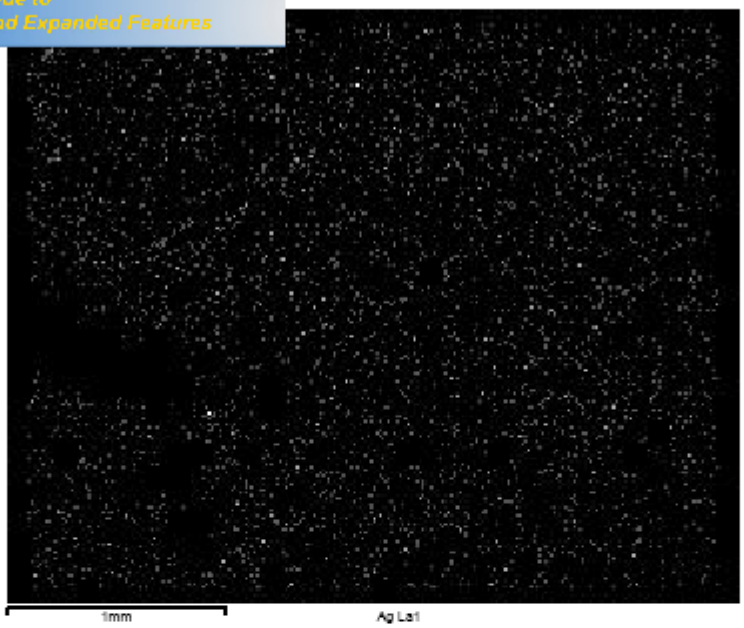
Element	Weight%	Atomic%
C K	12.58	35.18
O K	17.56	36.88
S K	5.39	5.65
Cu L	10.14	5.36
Ag L	54.34	16.93
Totals	100.00	

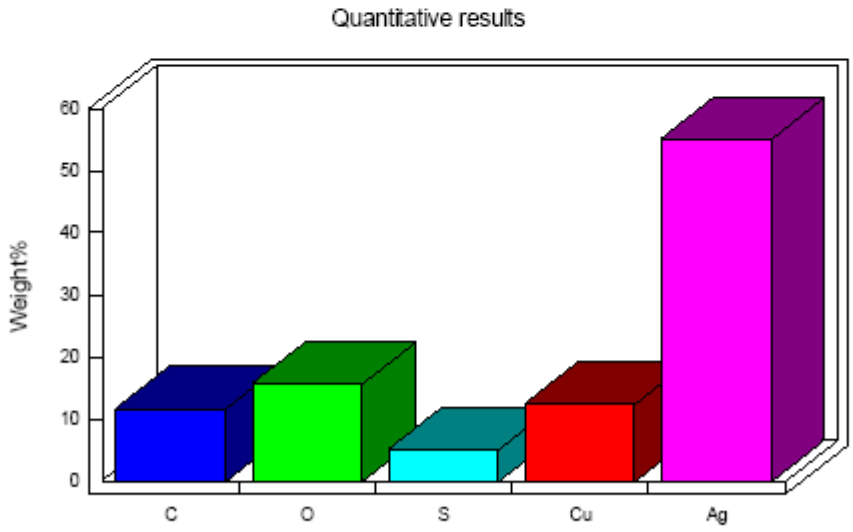
Comment: Medal 43 side 1 - PL side of background area 40 x

INCA

ESEM-EDX Results for Medal 43 side 1: silver (Ag) mapping - background area proper left side at 80x

8/19/2011 3:21:00 PM



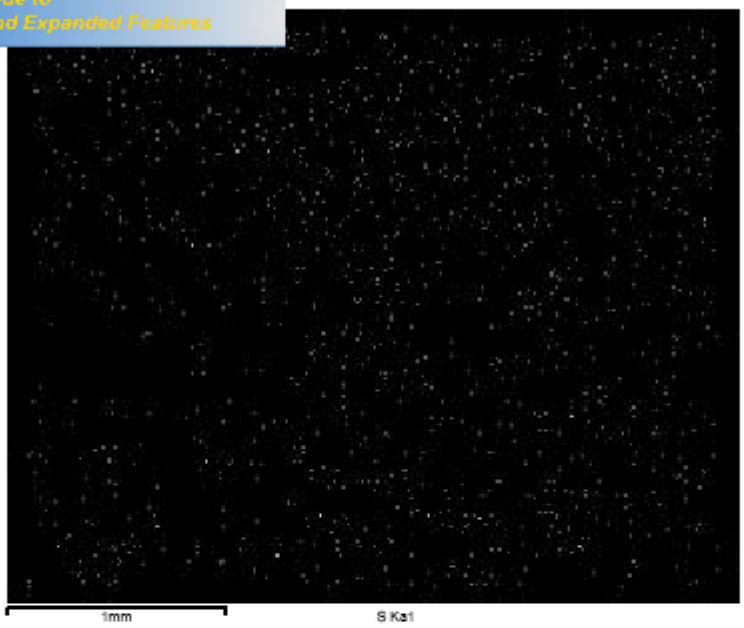


Comment: Medal 43 side 1 - PL hand of infant J. 80 x

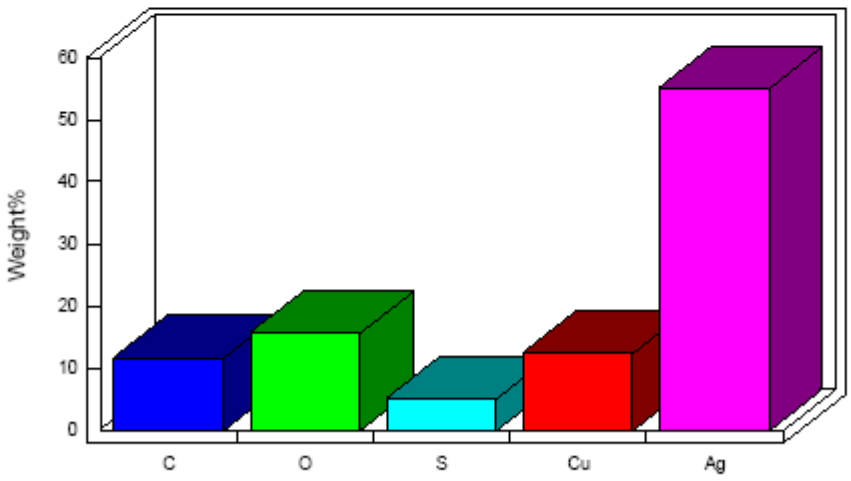
INCA

ESEM-EDX Results for Medal 43 side 1: sulphur (S) mapping - background area proper left side at 80x

8/19/2011 3:20:31 PM



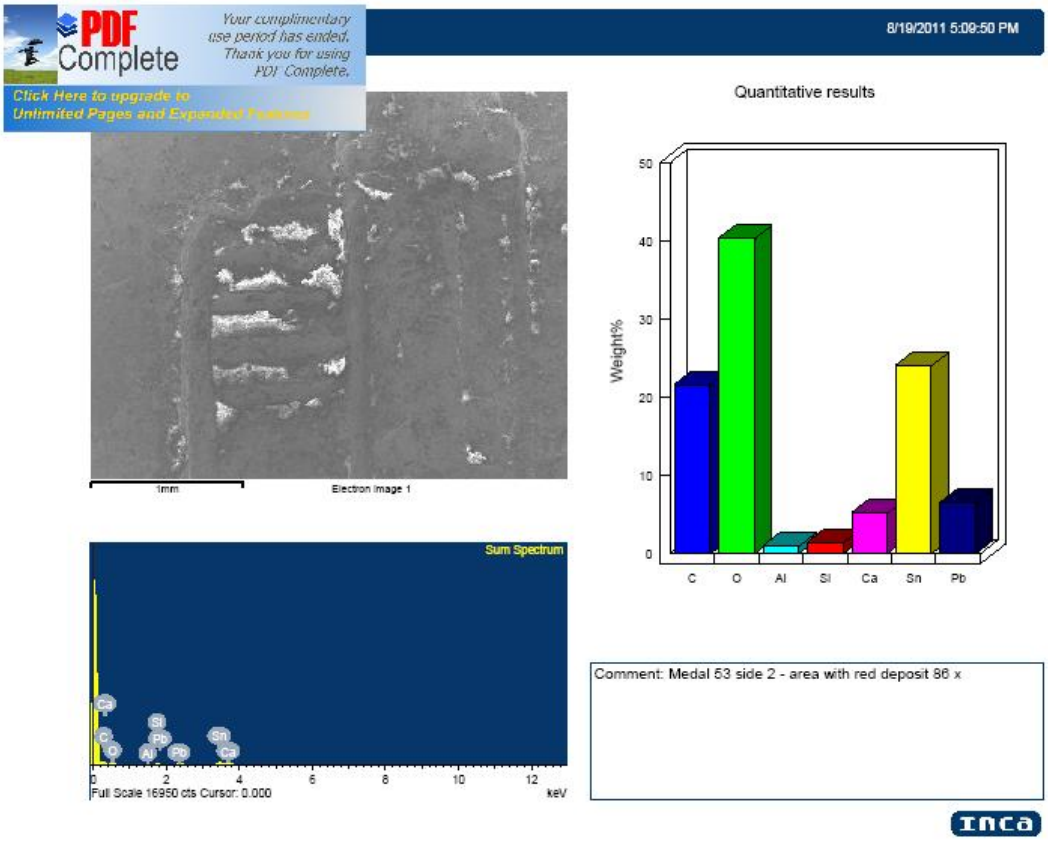
Quantitative results



Comment: Medal 43 side 1 - PL hand of infant J. 80 x

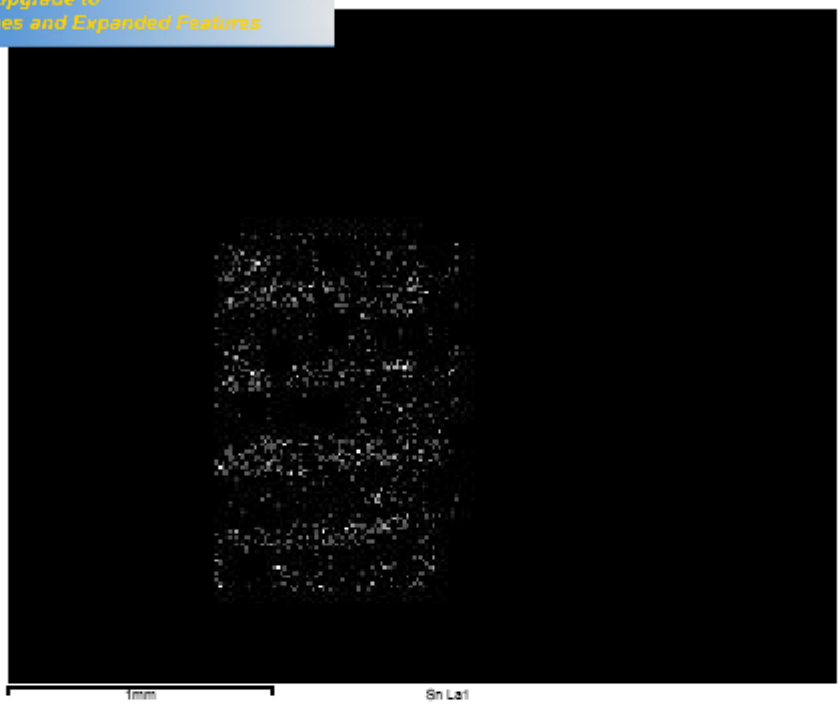
INCA

ESEM-EDX Results for Medal 53 side 2: area with red deposit at 86x



ESEM-EDX Results for Medal 53 side 2: tin (Sn) mapping - area with red deposit at 86x

8/19/2011 5:13:10 PM



Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 2

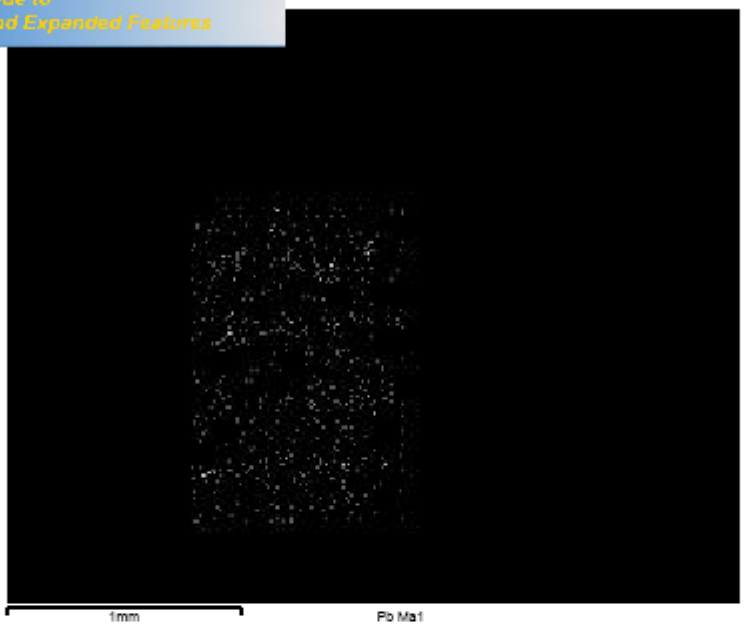
Standard :
C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
Al Al2O3 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
Ca Wollastonite 1-Jun-1999 12:00 AM
Sn Sn 1-Jun-1999 12:00 AM
Pb PbF2 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	21.61	37.74
O K	40.35	52.91
Al K	0.90	0.70
Si K	1.37	1.02
Ca K	5.18	2.71
Sn L	24.10	4.26
Pb M	6.50	0.66

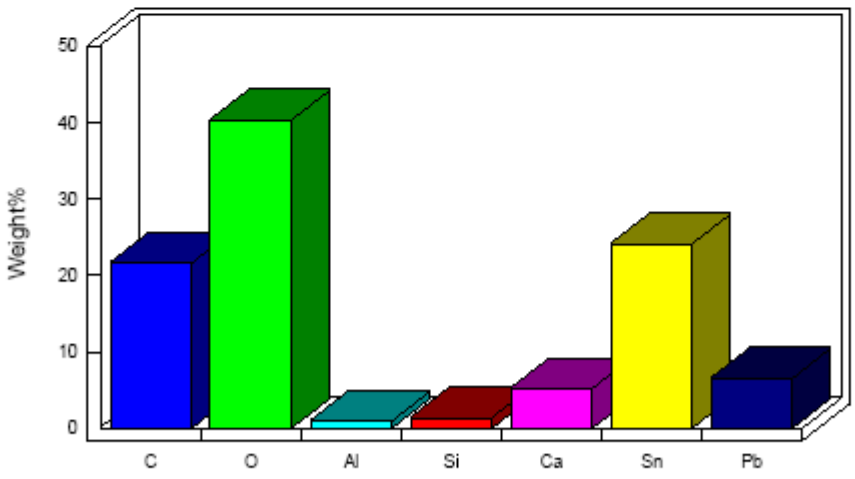
Comment: Medal 53 side 2 - area with red deposit 86 x

ESEM-EDX Results for Medal 53 side 2: lead (Pb) mapping - area with red deposit at 86x

8/19/2011 5:11:50 PM



Quantitative results



Comment: Medal 53 side 2 - area with red deposit 86 x

inca

ESEM-EDX Results for Medal 54 side 1: upper central area with the cross at 50x

8/25/2011 12:21:20 PM

Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 1

Standard :
Cu Cu 1-Jun-1999 12:00 AM
Zn Zn 1-Jun-1999 12:00 AM
Ag Ag 1-Jun-1999 12:00 AM

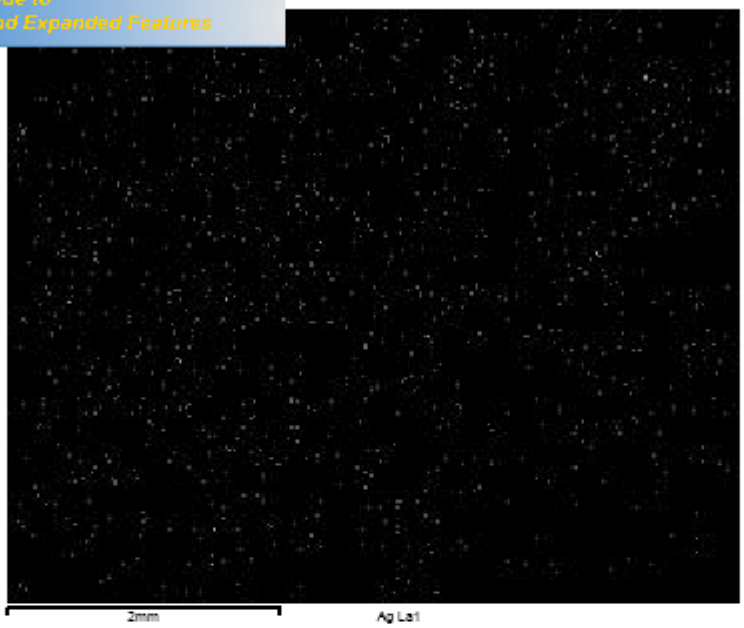
Element	Weight%	Atomic%
Cu K	57.06	62.59
Zn K	23.04	24.56
Ag L	19.90	12.86
Totals	100.00	

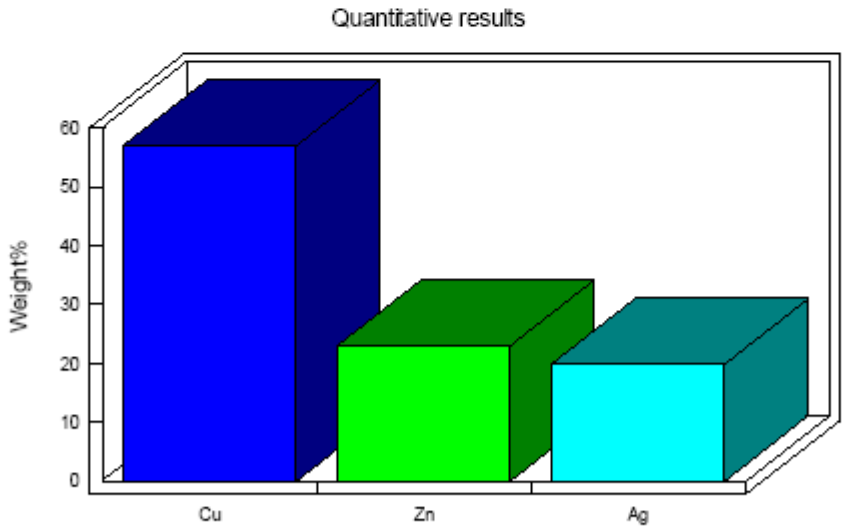
Comment: Medal 54 side 1 - area with the cross 50 x

INCA

ESEM-EDX Results for Medal 54 side 1: silver (Ag) mapping - upper central area with the cross at 50x

8/25/2011 12:22:26 PM





Comment: Medal 54 side 1 - area with the cross 50 x

INCA

ESEM-EDX Results for Medal 54 side 1: area with corrosion in the inscription 'DESCENDEZ' at 150x

8/25/2011 1:20:46 PM

Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 2

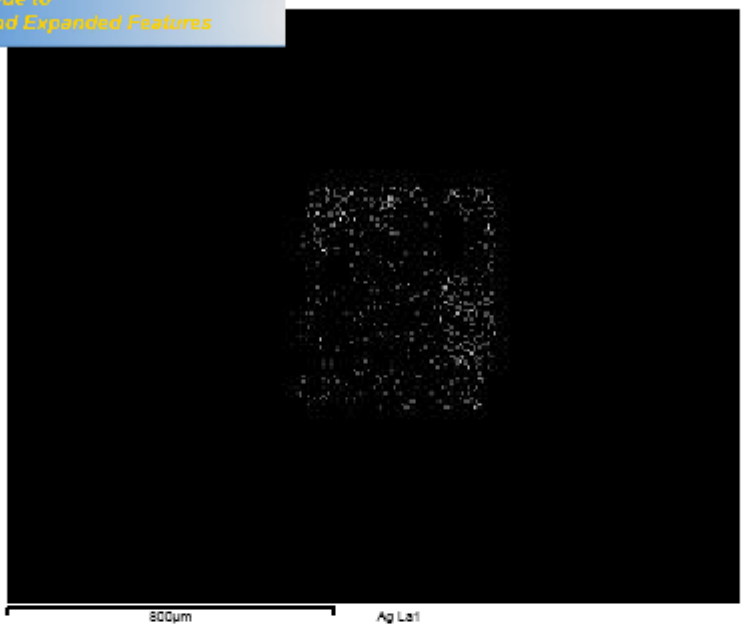
Standard :
O SiO2 1-Jun-1999 12:00 AM
S FeS2 1-Jun-1999 12:00 AM
Cl KCl 1-Jun-1999 12:00 AM
Cu Cu 1-Jun-1999 12:00 AM
Zn Zn 1-Jun-1999 12:00 AM
Ag Ag 1-Jun-1999 12:00 AM

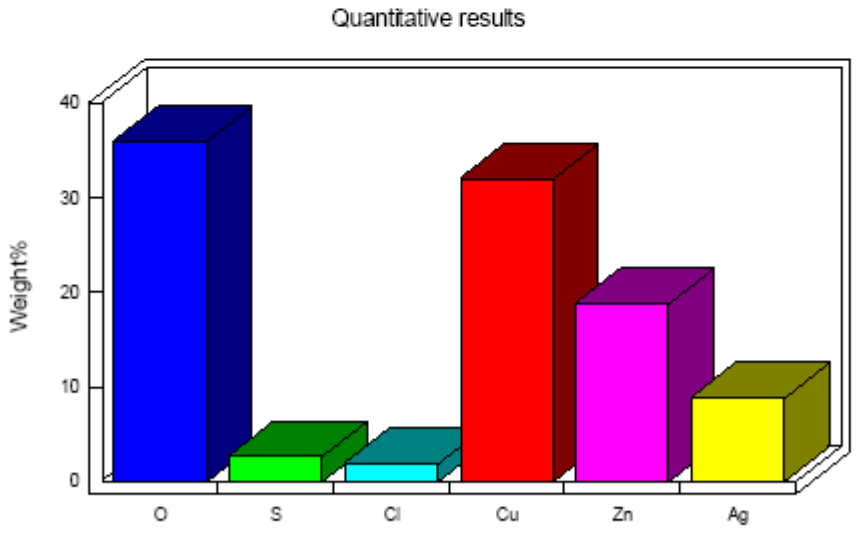
Element	Weight%	Atomic%
O K	35.94	69.05
S K	2.61	2.51
Cl K	1.87	1.62
Cu K	32.00	15.48
Zn K	18.77	8.83
Ag L	8.81	2.51
Totals	100.00	

Comment: Medal 54 side 1 - area with corrosion in inscription 'DESCENDEZ' 150 x

ESEM-EDX Results for Medal 54 side 1: silver (Ag) mapping - area with corrosion in the inscription 'DESCENDEZ' at 150x

8/25/2011 1:21:43 PM

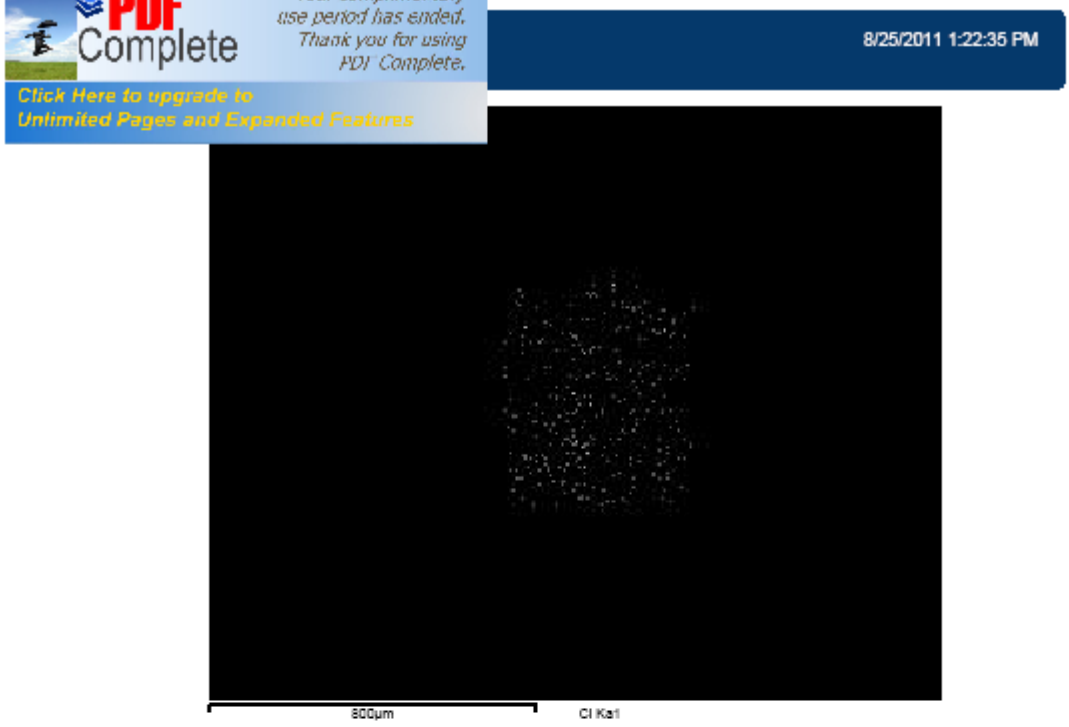


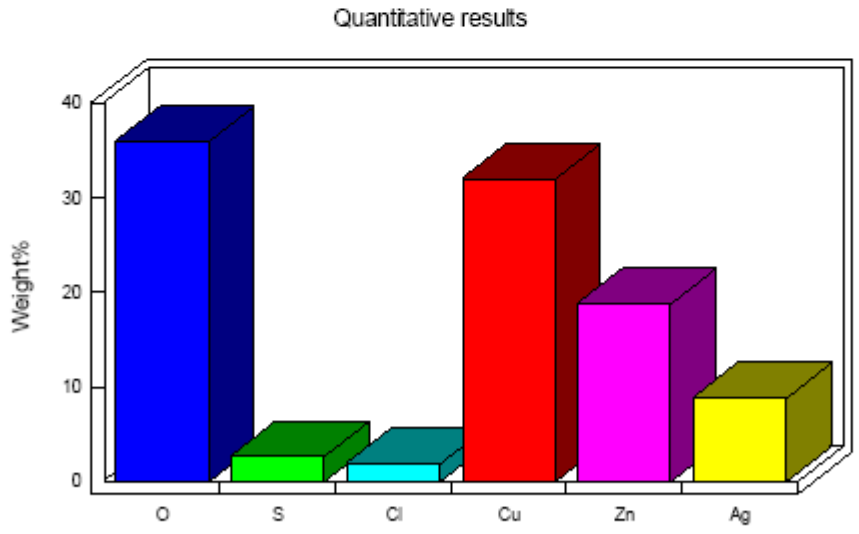


Comment: Medal 54 side 1 - area with corrosion in inscription 'DESCENDEZ' 150 x

inca

ESEM-EDX Results for Medal 54 side 1: chlorine (Cl) mapping - area with corrosion in the inscription 'DESCENDEZ' at 150x





Comment: Medal 54 side 1 - area with corrosion in inscription 'DESCENDEZ' 150 x

INCA

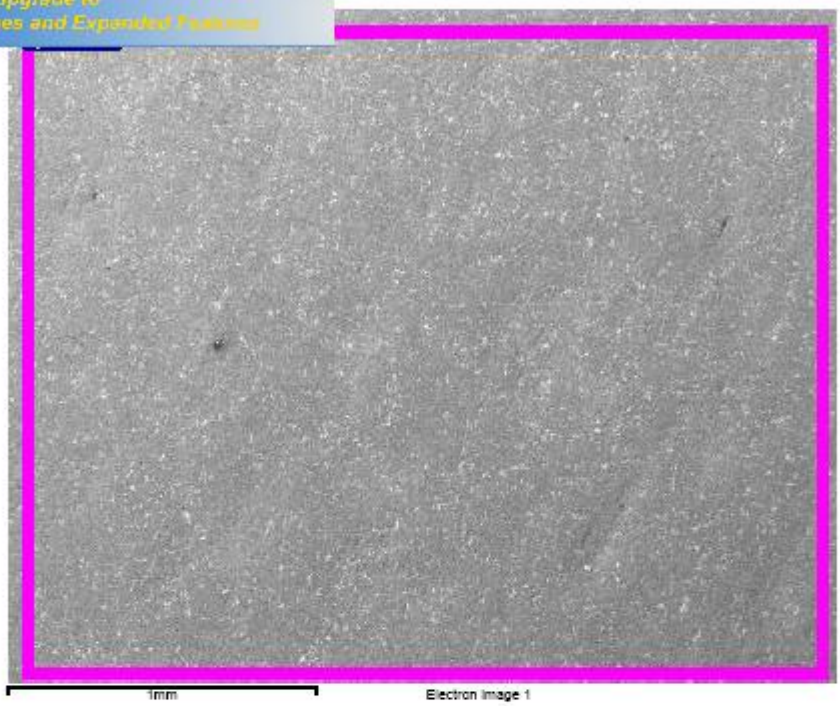
6.2 Analysing the Effects of Cleaning Treatments in Metals Conservation with Scanning Electron Microscopy - Energy Dispersive X-ray Spectroscopy

6.2.1 pXRF Results for the Silver, Copper, Lead and Iron Control Coupons

6.2.2 ESEM-EDX Results for the Silver Coupons at c. 100x

Ag I: Before Treatment at 100x

3/3/2011 1:55:38 PM



Spectrum processing :
Peak possibly omitted : 1.230 keV

Processing option : All elements analyzed (Normalised)
Number of iterations = 2

Standard :
C CaCO3 1-Jun-1999 12:00 AM
Ag Ag 1-Jun-1999 12:00 AM

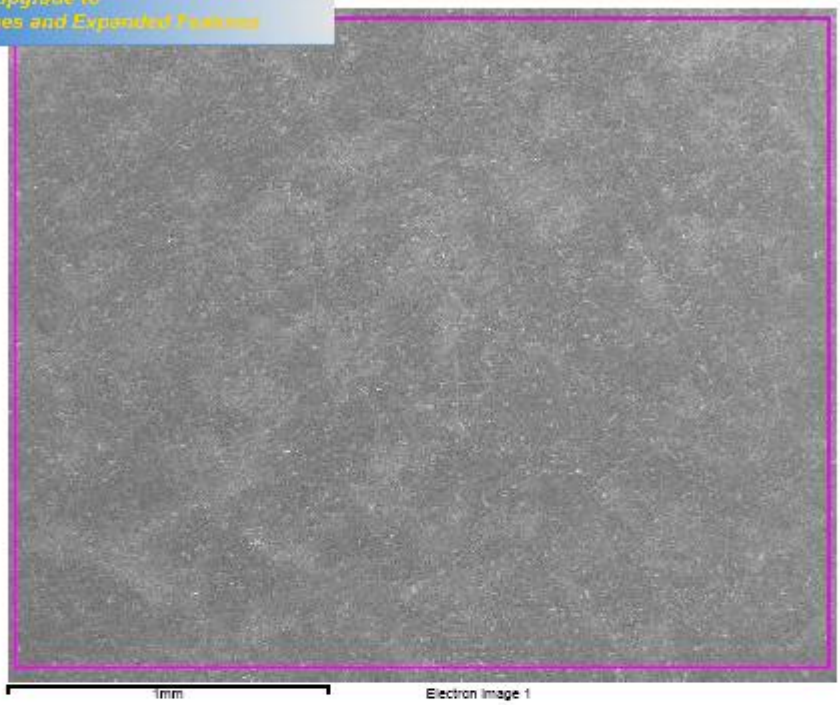
Element	Weight%	Atomic%
C K	3.26	23.23
Ag L	96.74	76.77
Totals	100.00	

Comment: Ag sample 1 - 100 X mag. - central area

inca

Ag I: After Treatment at 104x

3/16/2011 3:33:59 PM



Processing option : All elements analysed (Normalised)

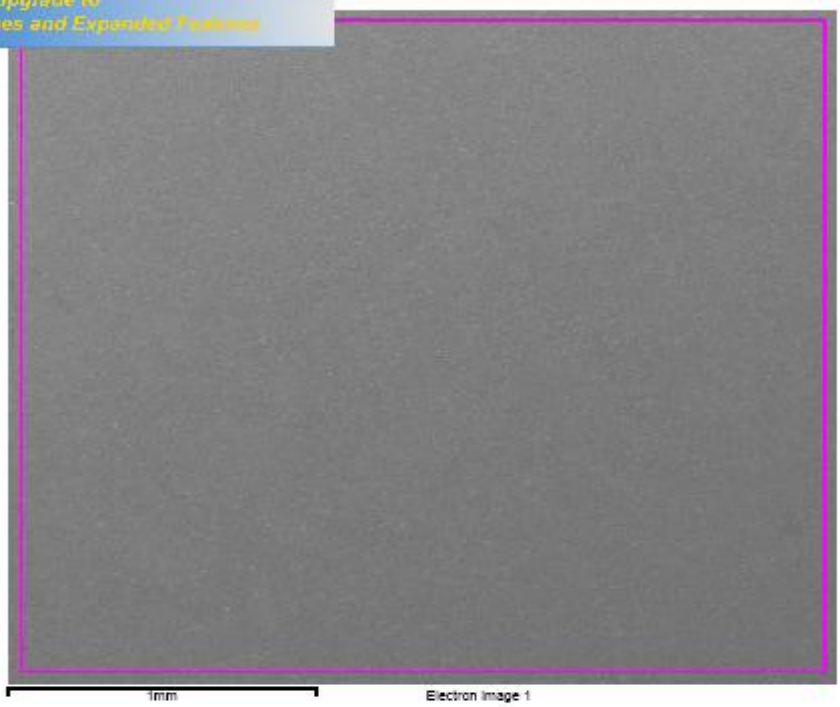
Spectrum	In stats.	C	Ag	Total
Spectrum 1	Yes	3.38	96.62	100.00
Mean		3.38	96.62	100.00
Std. deviation		0.00	0.00	
Max.		3.38	96.62	
Min.		3.38	96.62	

All results in weight%

inca

Ag I: 2 Months After Treatment at 100x

5/16/2011 12:17:57 PM



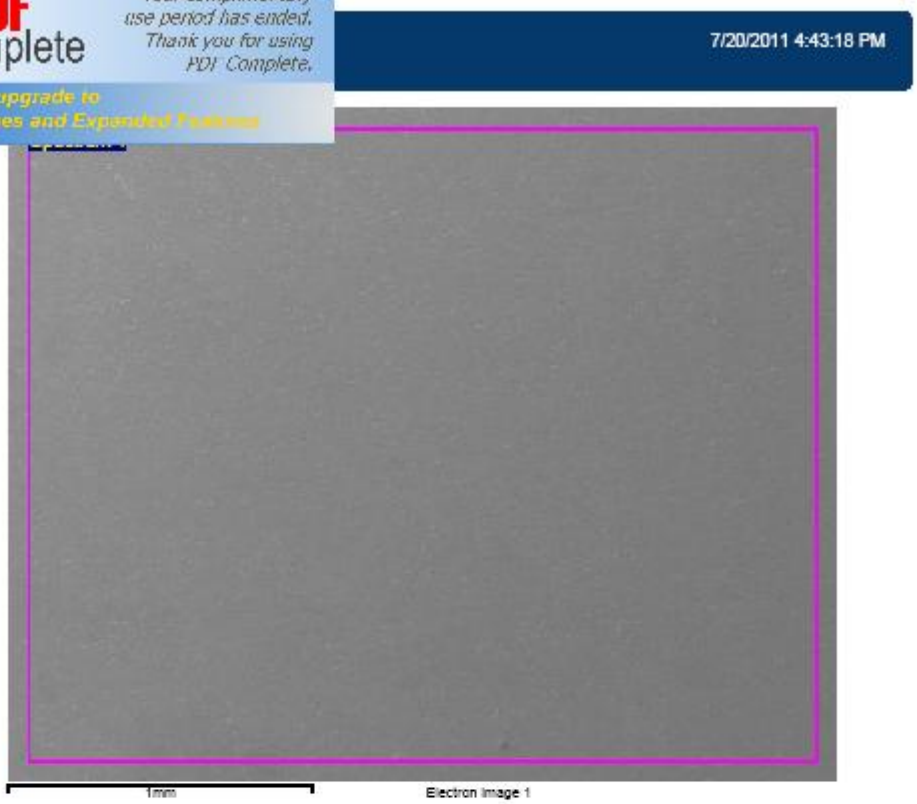
Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	Ag	Total
Spectrum 1	Yes	3.23	96.77	100.00
Mean		3.23	96.77	100.00
Std. deviation		0.00	0.00	
Max.		3.23	96.77	
Min.		3.23	96.77	

All results in weight%

inca

Ag I: 4 Months After Treatment at 100x



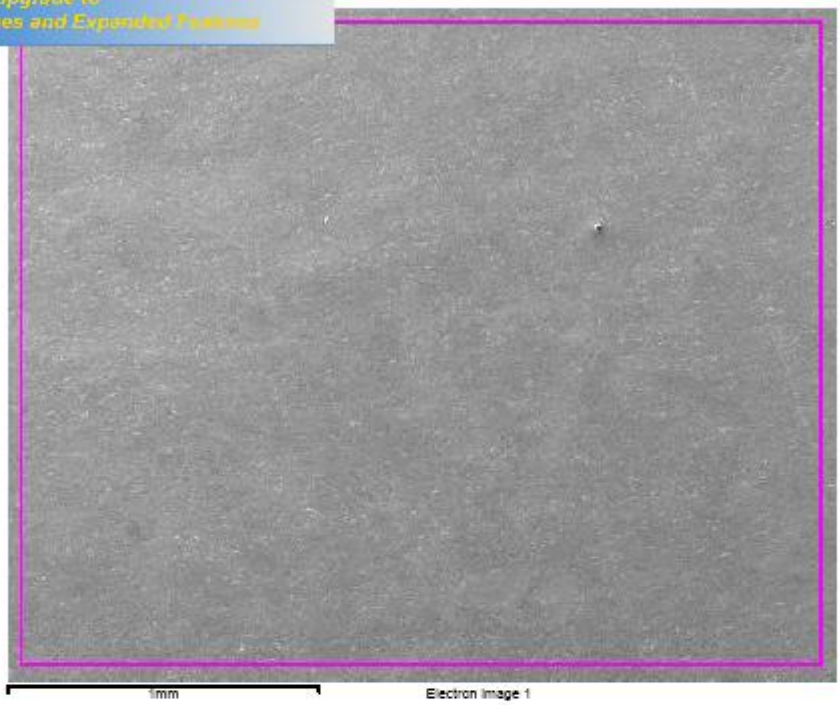
Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	Ag	Total
Spectrum 1	Yes	2.42	97.58	100.00
Mean		2.42	97.58	100.00
Std. deviation		0.00	0.00	
Max.		2.42	97.58	
Min.		2.42	97.58	

All results in weight%

Ag I: 6 Months After Treatment at 100x

9/28/2011 3:46:29 PM



Processing option : All elements analysed (Normalised)

Spectrum	In stats.	Ag	Total
Spectrum 1	Yes	100.00	100.00
Mean		100.00	100.00
Std. deviation		0.00	
Max.		100.00	
Min.		100.00	

All results in weight%

inca

Ag II: Before Treatment at 100x

3/3/2011 2:46:20 PM

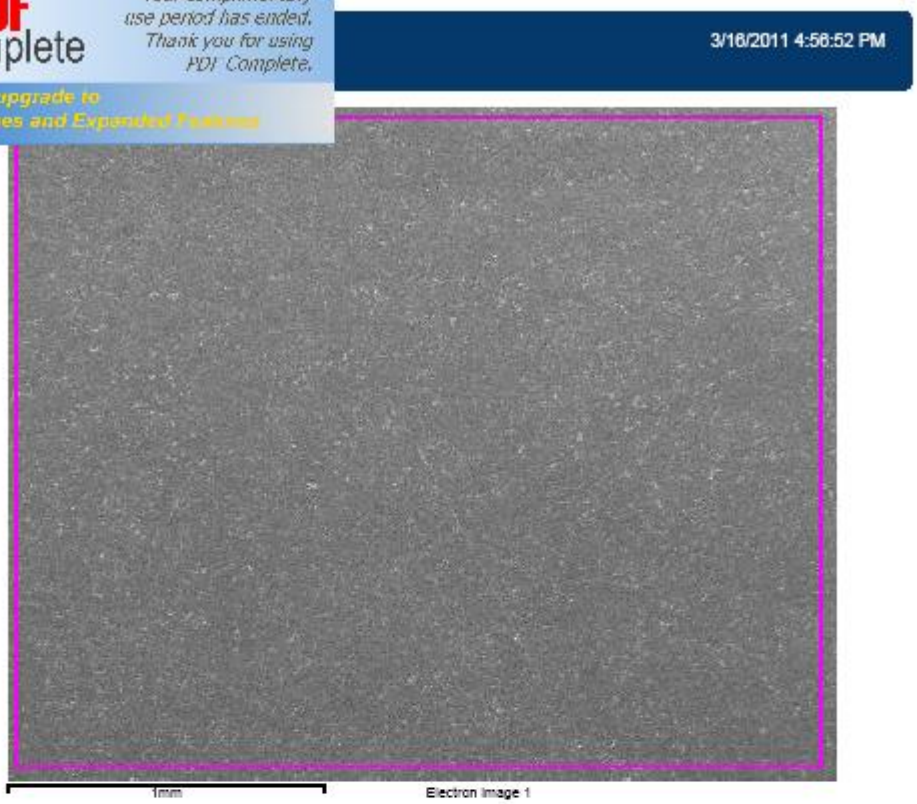
Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	Ag	Total
Spectrum 1	Yes	3.64	96.36	100.00
Mean		3.64	96.36	100.00
Std. deviation		0.00	0.00	
Max.		3.64	96.36	
Min.		3.64	96.36	

All results in weight%

inca

Ag II: After Treatment at 103x



Processing option : All elements analysed (Normalised)

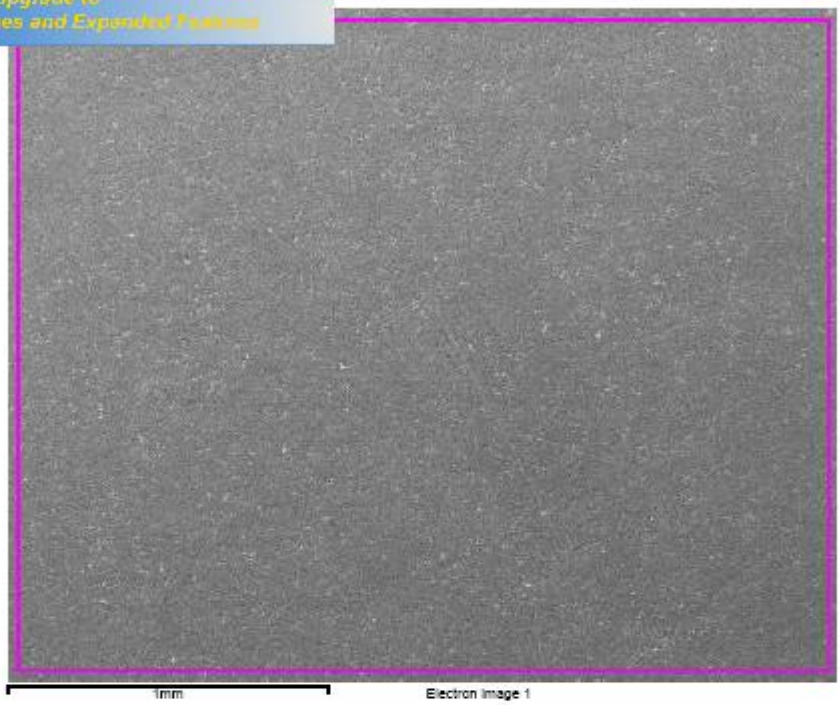
Spectrum	In stats.	C	Ag	Total
Spectrum 1	Yes	3.88	96.12	100.00
Mean		3.88	96.12	100.00
Std. deviation		0.00	0.00	
Max.		3.88	96.12	
Min.		3.88	96.12	

All results in weight%

inca

Ag II: 2 Months After Treatment at 104x

5/16/2011 3:14:31 PM



Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	Ag	Total
Spectrum 1	Yes	3.99	96.01	100.00
Mean		3.99	96.01	100.00
Std. deviation		0.00	0.00	
Max.		3.99	96.01	
Min.		3.99	96.01	

All results in weight%

inca

Ag II: 4 Months After Treatment at 100x

7/20/2011 4:53:25 PM

Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	Ag	Total
Spectrum 1	Yes	2.20	97.80	100.00
Mean		2.20	97.80	100.00
Std. deviation		0.00	0.00	
Max.		2.20	97.80	
Min.		2.20	97.80	

All results in weight%

inca

Ag II: 6 Months After Treatment at 104x

9/28/2011 4:32:24 PM

Processing option : All elements analysed (Normalised)

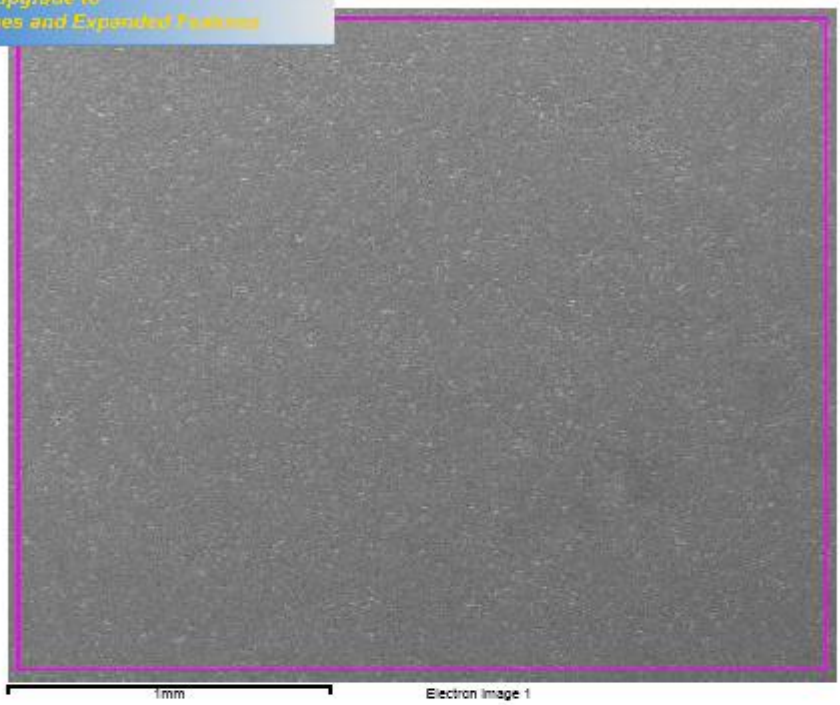
Spectrum	In stats.	C	Ag	Total
Spectrum 1	Yes	1.16	98.84	100.00
Mean		1.16	98.84	100.00
Std. deviation		0.00	0.00	
Max.		1.16	98.84	
Min.		1.16	98.84	

All results in weight%

inca

Ag III: Before Treatment at 105x

5/6/2011 11:36:55 AM



Processing option : All elements analysed (Normalised)

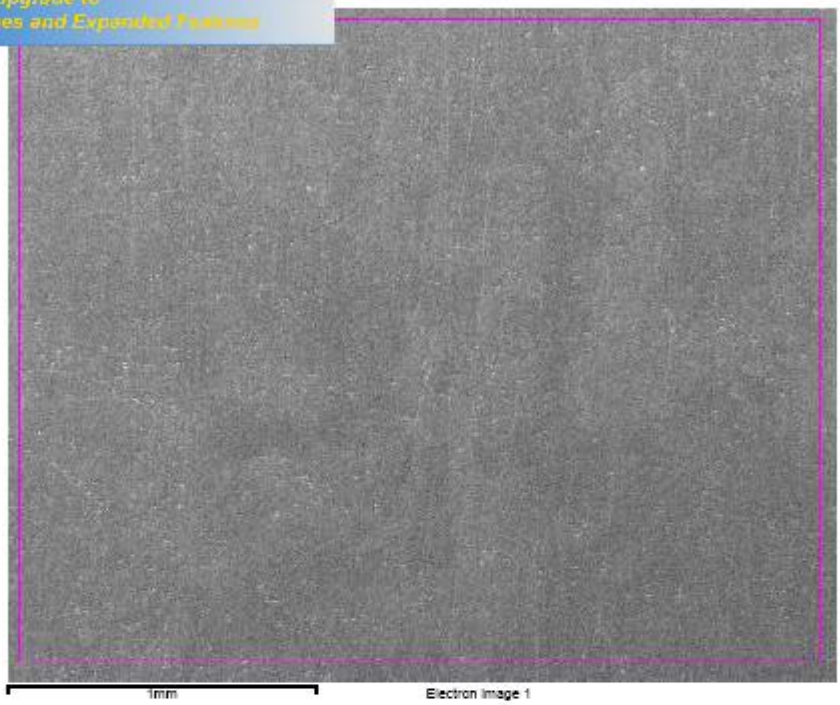
Spectrum	In stats.	C	Ag	Total
Spectrum 1	Yes	4.13	95.87	100.00
Mean		4.13	95.87	100.00
Std. deviation		0.00	0.00	
Max.		4.13	95.87	
Min.		4.13	95.87	

All results in weight%

inca

Ag III: After Treatment at 101x

5/9/2011 3:15:15 PM



Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 2

Standard :
C CaCO3 1-Jun-1999 12:00 AM
Ag Ag 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	4.21	28.28
Ag L	95.79	71.72
Totals	100.00	

Comment:
Ag III A.T. 101 x

inca

Ag III: 2 Months After Treatment at 101x

7/20/2011 11:29:11 AM

Spectrum processing :
Peak possibly omitted : 1.770 keV

Processing option : All elements analyzed (Normalised)
Number of iterations = 2

Standard :
C CaCO3 1-Jun-1999 12:00 AM
Ag Ag 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	2.32	17.60
Ag L	97.68	82.40
Totals	100.00	

Comment:
Ag III A.T. 101x - 2 mths

inca

Ag III: 4 Months After Treatment at 101x

9/28/2011 5:24:34 PM

Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	Ag	Total
Spectrum 1	Yes	1.66	98.34	100.00
Mean		1.66	98.34	100.00
Std. deviation		0.00	0.00	
Max.		1.66	98.34	
Min.		1.66	98.34	

All results in weight%

inca

Ag III: 6 Months After Treatment at 102x

11/21/2011 2:18:15 PM

Processing option : All elements analysed (Normalised)

Spectrum	In stats.	Ag	Total
Spectrum 1	Yes	100.00	100.00
Mean		100.00	100.00
Std. deviation		0.00	
Max.		100.00	
Min.		100.00	

All results in weight%

inca

Ag IV: Control at 104x

9/28/2011 5:54:42 PM

Processing option : All elements analysed (Normalised)

Spectrum	In stats.	Ag	Total
Spectrum 1	Yes	100.00	100.00
Mean		100.00	100.00
Std. deviation		0.00	
Max.		100.00	
Min.		100.00	

All results in weight%

inca

6.2.3 ESEM-EDX Results for the Copper Coupons at c. 100x

Cu I: After Treatment at 101x

3/16/2011 11:19:10 AM

Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	Cu	Total
Spectrum 1	Yes	11.31	88.69	100.00
Mean		11.31	88.69	100.00
Std. deviation		0.00	0.00	
Max.		11.31	88.69	
Min.		11.31	88.69	

All results in weight%

INCA

Cu I: 2 Months After Treatment at 103x

5/18/2011 12:45:38 PM

Processing option : All elements analysed (Normalised)

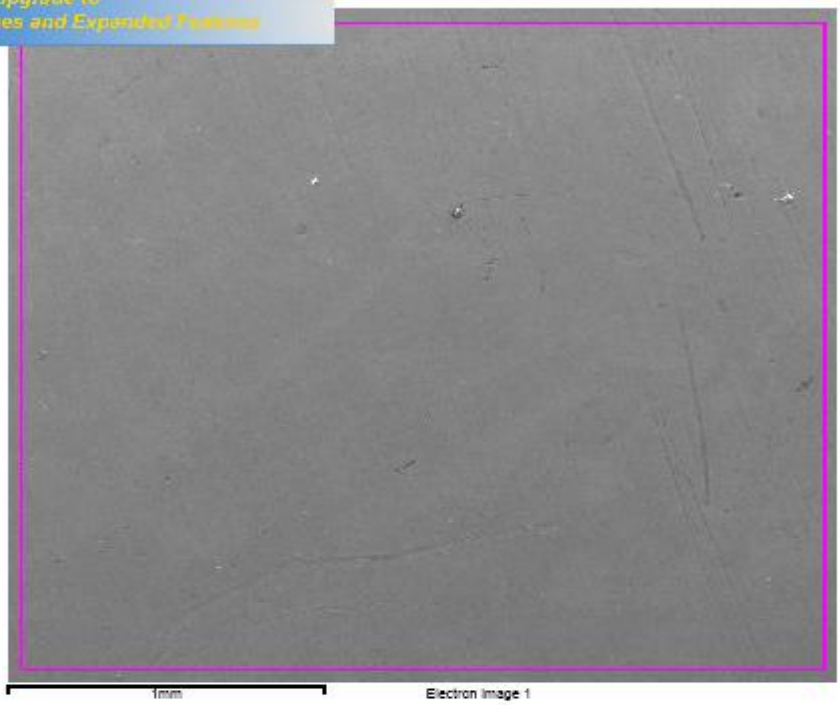
Spectrum	In stats.	C	Cu	Total
Spectrum 1	Yes	10.46	89.54	100.00
Mean		10.46	89.54	100.00
Std. deviation		0.00	0.00	
Max.		10.46	89.54	
Min.		10.46	89.54	

All results in weight%

inca

Cu I: 4 Months After Treatment at 103x

7/20/2011 5:26:00 PM



Processing option : All elements analysed (Normalised)

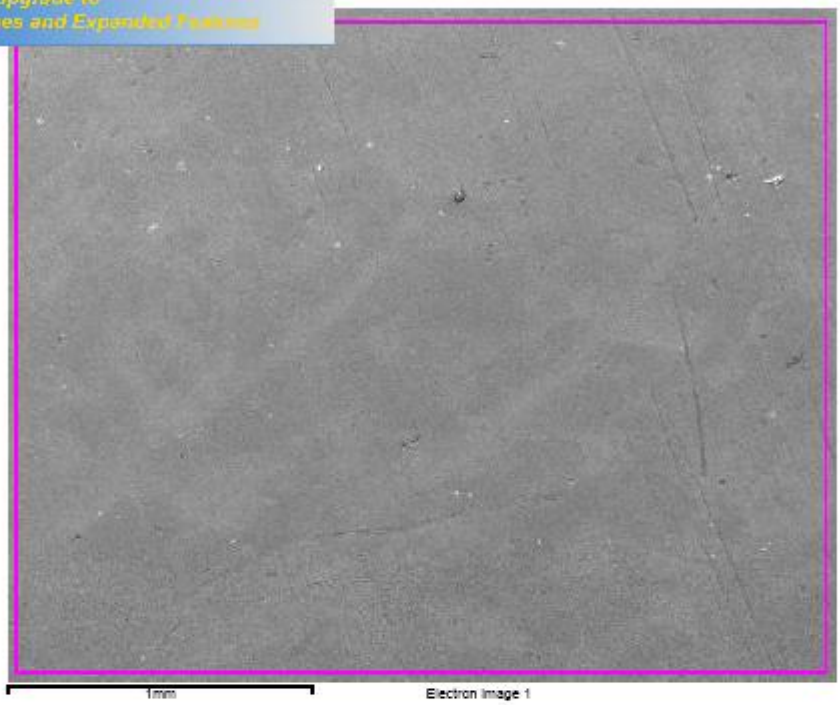
Spectrum	In stats.	C	O	Cu	Total
Spectrum 1	Yes	9.20	1.03	89.76	100.00
Mean		9.20	1.03	89.76	100.00
Std. deviation		0.00	0.00	0.00	
Max.		9.20	1.03	89.76	
Min.		9.20	1.03	89.76	

All results in weight%

inca

Cu I: 6 Months After Treatment at 100x

9/28/2011 11:11:01 AM



Processing option : All elements analysed (Normalised)

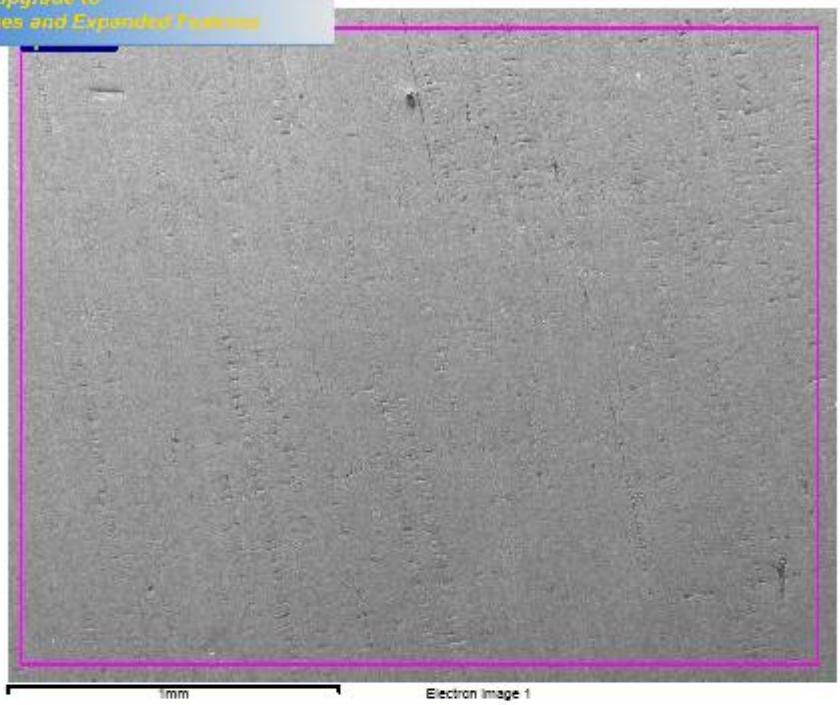
Spectrum	In stats.	O	Cu	Total
Spectrum 1	Yes	2.16	97.84	100.00
Mean		2.16	97.84	100.00
Std. deviation		0.00	0.00	
Max.		2.16	97.84	
Min.		2.16	97.84	

All results in weight%

inca

Cu II: Before Treatment at 107x

3/3/2011 12:35:00 PM



Spectrum processing :
Peak possibly omitted : 14.180 keV

Processing option : All elements analyzed (Normalised)
Number of iterations = 2

Standard :
C CaCO3 1-Jun-1999 12:00 AM
Cu Cu 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	8.06	31.70
Cu K	91.94	68.30
Totals	100.00	

Comment: Cu sample II - 107 X mag. - central area

inca

Cu II: After Treatment at 101x

3/16/2011 12:58:32 PM

Processing option : All elements analysed (Normalised)

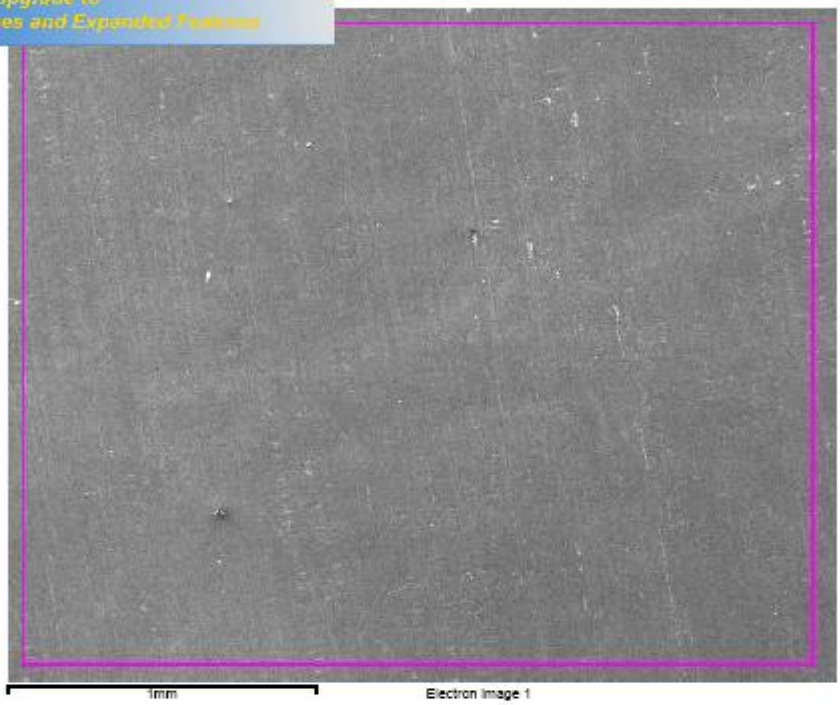
Spectrum	In stats.	Cu	Total
Spectrum 1	Yes	100.00	100.00
Mean		100.00	100.00
Std. deviation		0.00	
Max.		100.00	
Min.		100.00	

All results in weight%

inca

Cu II: 2 Months After Treatment at 101x

5/18/2011 1:39:27 PM



Processing option : All elements analysed (Normalised)

Spectrum	In stats.	O	Cu	Total
Spectrum 1	Yes	1.79	98.21	100.00
Mean		1.79	98.21	100.00
Std. deviation		0.00	0.00	
Max.		1.79	98.21	
Min.		1.79	98.21	

All results in weight%

inca

Cu II: 4 Months After Treatment at 101x

7/20/2011 6:03:00 PM

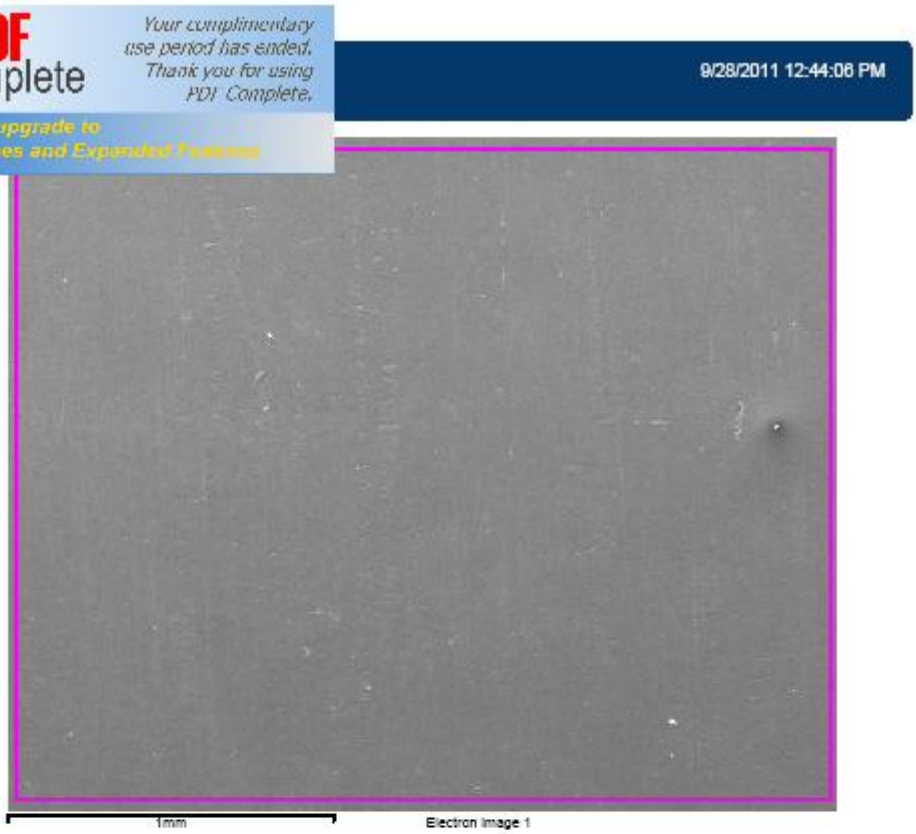
Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	O	Cu	Total
Spectrum 1	Yes	7.37	1.31	91.31	100.00
Mean		7.37	1.31	91.31	100.00
Std. deviation		0.00	0.00	0.00	
Max.		7.37	1.31	91.31	
Min.		7.37	1.31	91.31	

All results in weight%

inca

Cu II: 6 Months After Treatment at 106x



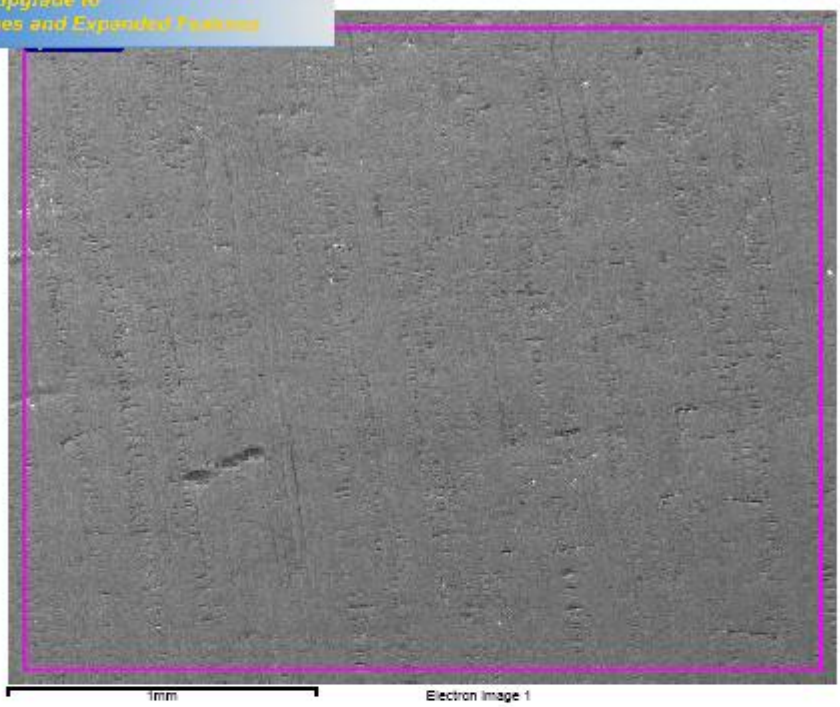
Processing option : All elements analysed (Normalised)

Spectrum	In stats.	O	Cu	Total
Spectrum 1	Yes	1.90	98.10	100.00
Mean		1.90	98.10	100.00
Std. deviation		0.00	0.00	
Max.		1.90	98.10	
Min.		1.90	98.10	

All results in weight%

Cu III: Before Treatment at 101x

3/3/2011 1:12:26 PM



Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 2

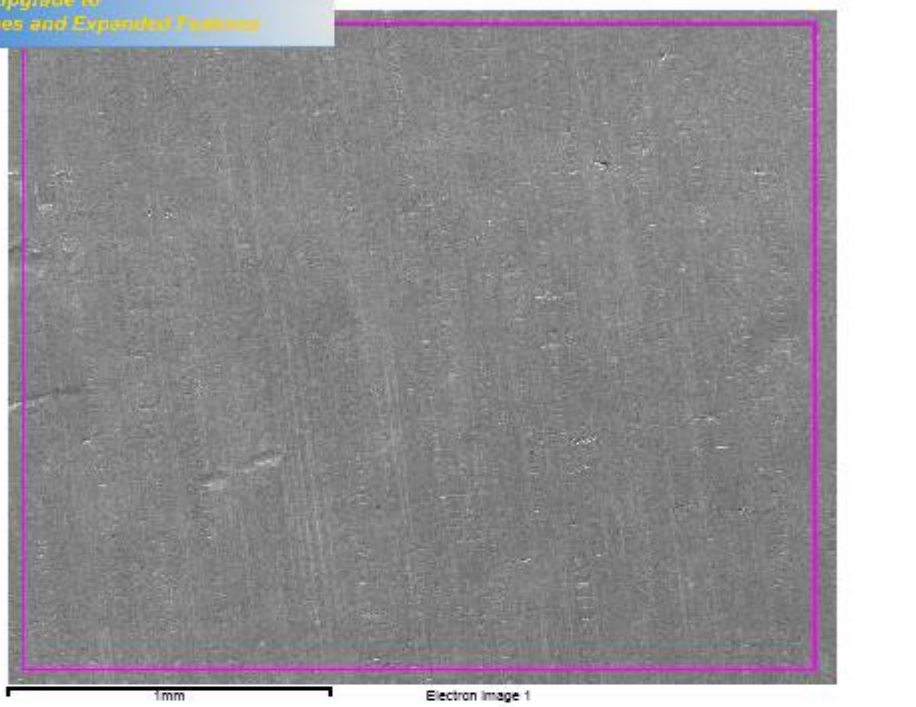
Standard :
C CaCO3 1-Jun-1999 12:00 AM
Cu Cu 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	8.50	32.95
Cu K	91.50	67.05
Totals	100.00	

Comment: Cu sample III - 101 X mag. - central area of sample

inca

Cu III: After Treatment at 105x



Processing option : All elements analysed (Normalised)

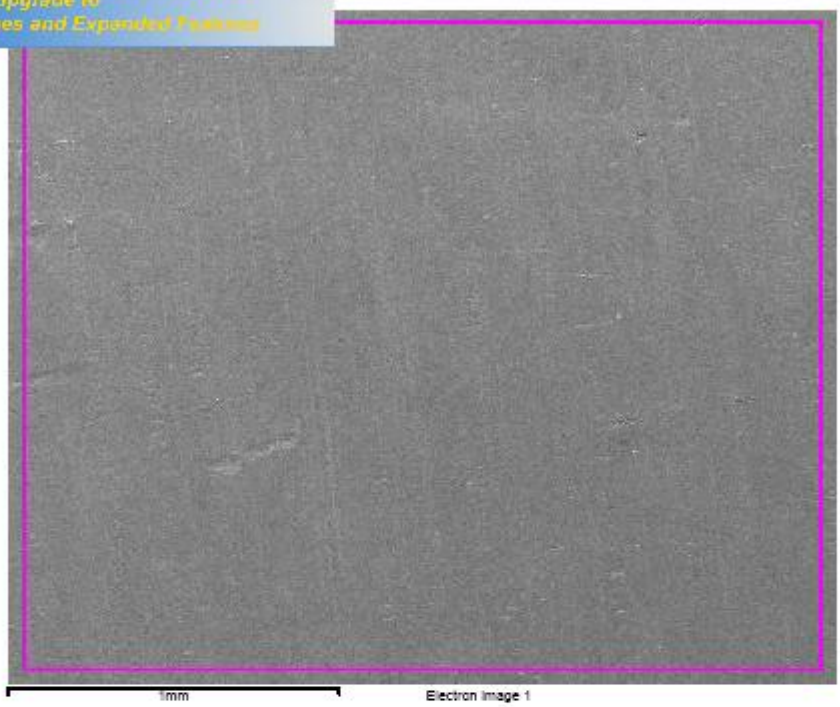
Spectrum	In stats.	C	O	Cu	Total
Spectrum 1	Yes	7.41	1.19	91.40	100.00
Mean		7.41	1.19	91.40	100.00
Std. deviation		0.00	0.00	0.00	
Max.		7.41	1.19	91.40	
Min.		7.41	1.19	91.40	

All results in weight%

inca

Cu III: 2 Months After Treatment at 108x

5/18/2011 3:25:32 PM



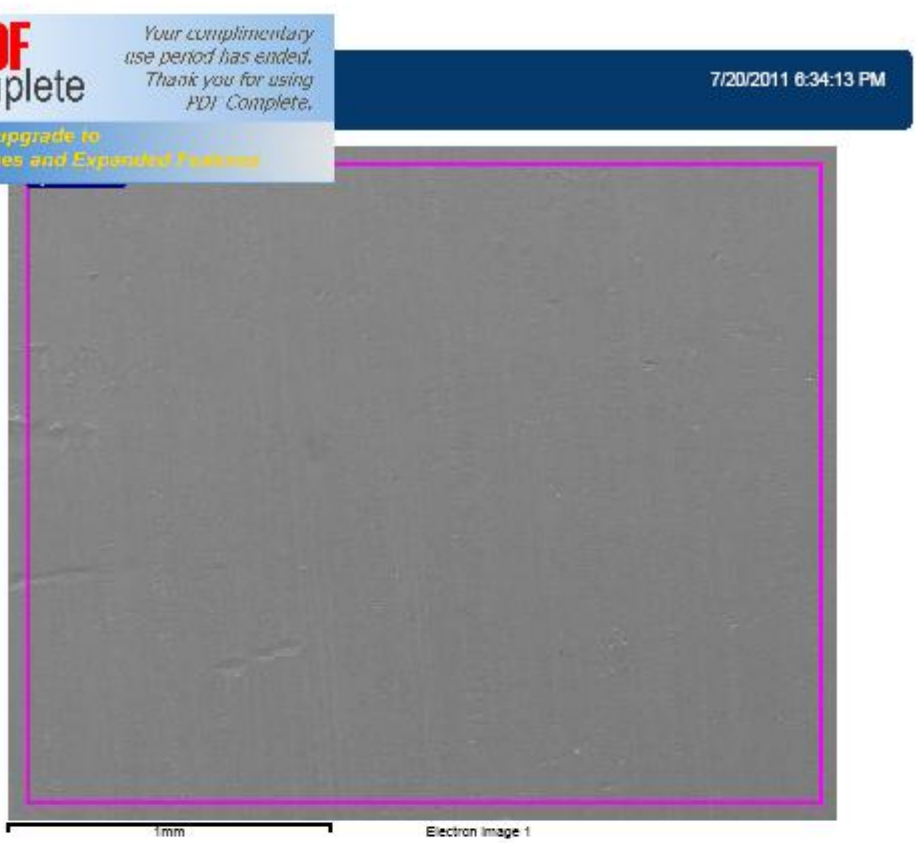
Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	O	Cu	Total
Spectrum 1	Yes	9.04	1.53	89.43	100.00
Mean		9.04	1.53	89.43	100.00
Std. deviation		0.00	0.00	0.00	
Max.		9.04	1.53	89.43	
Min.		9.04	1.53	89.43	

All results in weight%

inca

Cu III: 4 Months After Treatment at 105x



Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	O	Cu	Total
Spectrum 1	Yes	7.13	1.31	91.56	100.00
Mean		7.13	1.31	91.56	100.00
Std. deviation		0.00	0.00	0.00	
Max.		7.13	1.31	91.56	
Min.		7.13	1.31	91.56	

All results in weight%

Cu III: 6 Months After Treatment at 102x

Processing option : All elements analysed (Normalised)

Spectrum	In stats.	O	Cu	Total
Spectrum 1	Yes	1.74	98.26	100.00
Mean		1.74	98.26	100.00
Std. deviation		0.00	0.00	
Max.		1.74	98.26	
Min.		1.74	98.26	

All results in weight%

inca

Cu IV: Control at 106x

9/28/2011 1:43:42 PM

Processing option : All elements analysed (Normalised)

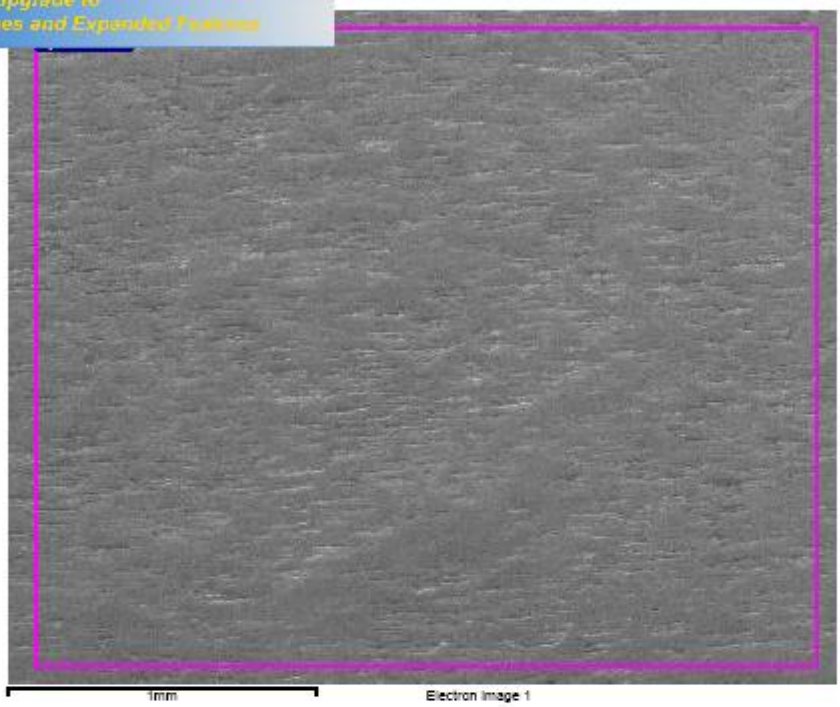
Spectrum	In stats.	Cu	Total
Spectrum 1	Yes	100.00	100.00
Mean		100.00	100.00
Std. deviation		0.00	
Max.		100.00	
Min.		100.00	

All results in weight%

6.2.4 ESEM-EDX Results for the Lead Coupons c. 100x

Pb I: Before Treatment at 100x

3/10/2011 11:31:15 AM



Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 3

Standard :
C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
Pb PbF2 1-Jun-1999 12:00 AM

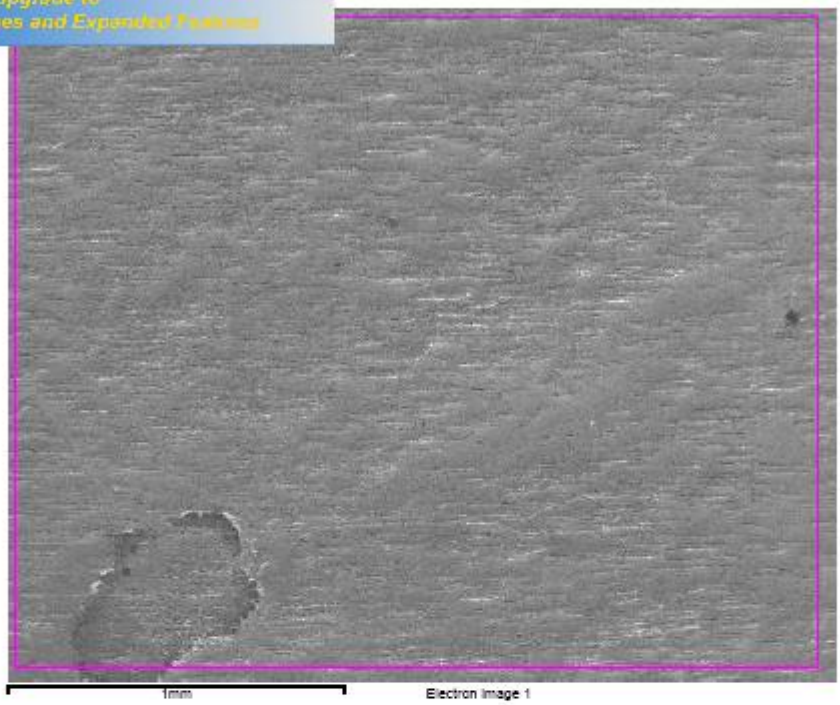
Element	Weight%	Atomic%
C K	15.09	48.78
O K	14.77	35.85
Si K	1.86	2.57
Pb M	68.28	12.80
Totals	100.00	

Comment: Pb I B.T. 100 x mag.

inca

Pb I: After Treatment at 110x

3/24/2011 2:11:45 PM



Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 2

Standard :
C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
Pb PbF2 1-Jun-1999 12:00 AM

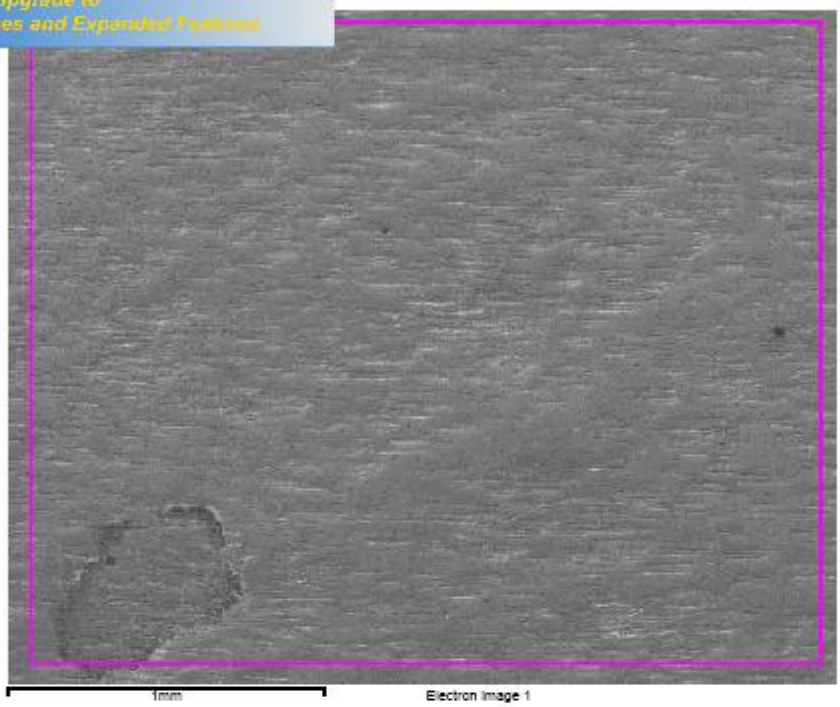
Element	Weight%	Atomic%
C K	13.52	61.21
O K	5.13	17.44
Pb M	81.35	21.35
Totals	100.00	

Comment: Pb I A.T. 110 x mag.

inca

Pb I: 2 Months After Treatment at 103x

5/6/2011 12:33:49 PM



Processing option : All elements analysed (Normalised)

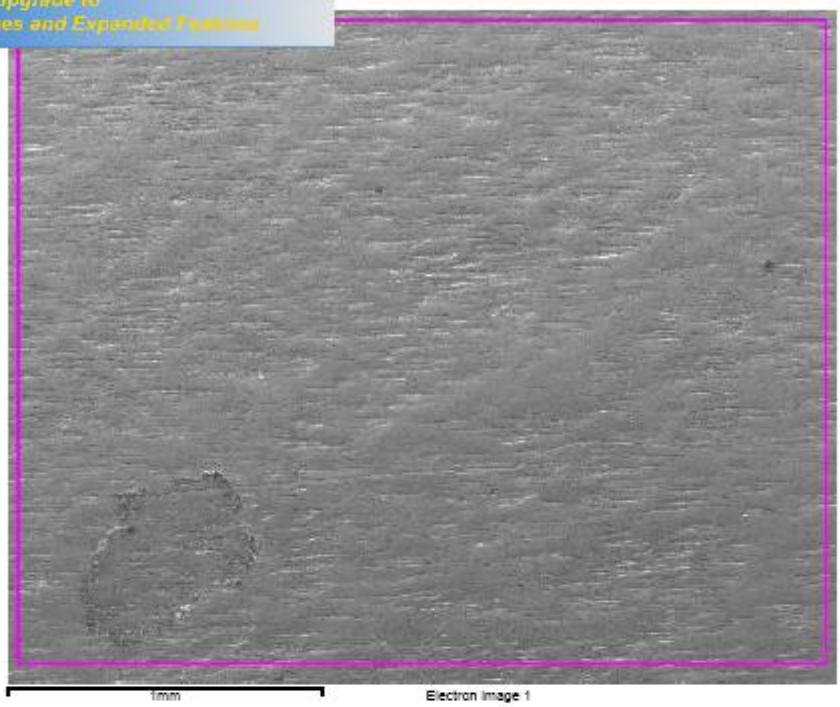
Spectrum	In stats.	C	O	Pb	Total
Spectrum 1	Yes	13.64	6.64	79.73	100.00
Mean		13.64	6.64	79.73	100.00
Std. deviation		0.00	0.00	0.00	
Max.		13.64	6.64	79.73	
Min.		13.64	6.64	79.73	

All results in weight%

inca

Pb I: 4 Months After Treatment at 102x

7/21/2011 10:48:43 AM



Processing option : All elements analysed (Normalised)

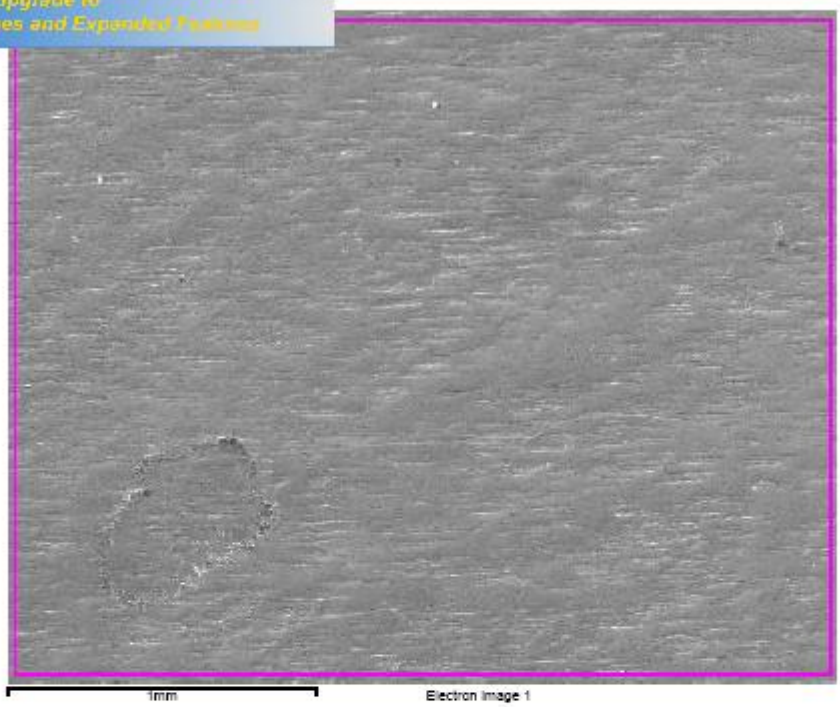
Spectrum	In stats.	C	O	Pb	Total
Spectrum 1	Yes	10.73	8.96	80.30	100.00
Mean		10.73	8.96	80.30	100.00
Std. deviation		0.00	0.00	0.00	
Max.		10.73	8.96	80.30	
Min.		10.73	8.96	80.30	

All results in weight%

inca

Pb I: 6 Months After Treatment at 100x

9/30/2011 2:24:12 PM



Processing option : All elements analysed (Normalised)

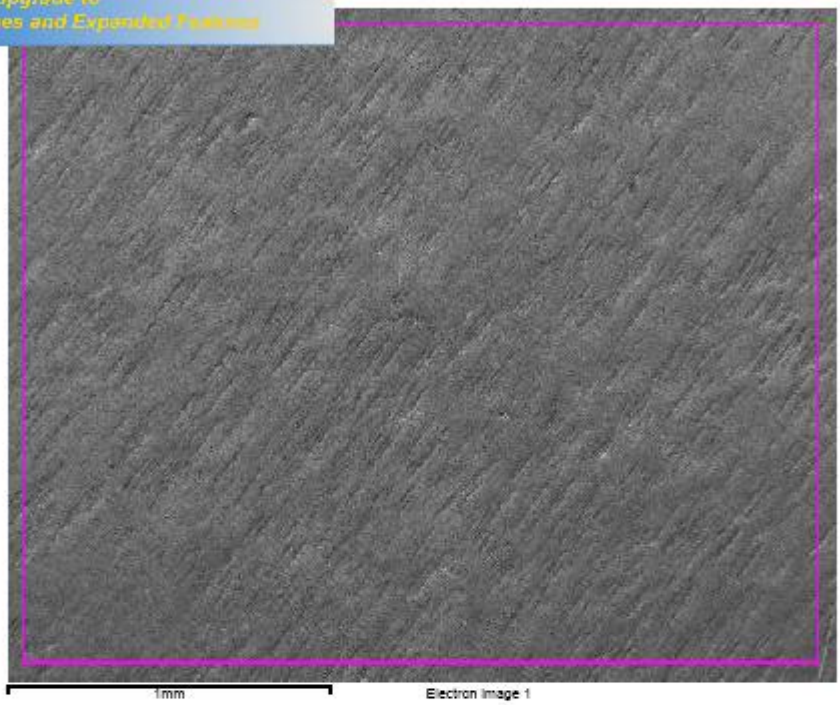
Spectrum	In stats.	C	O	Pb	Total
Spectrum 1	Yes	10.85	10.28	78.87	100.00
Mean		10.85	10.28	78.87	100.00
Std. deviation		0.00	0.00	0.00	
Max.		10.85	10.28	78.87	
Min.		10.85	10.28	78.87	

All results in weight%

inca

Pb II: Before Treatment at 105x

3/10/2011 12:12:00 PM



Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 3

Standard :
C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
Pb PbF2 1-Jun-1999 12:00 AM

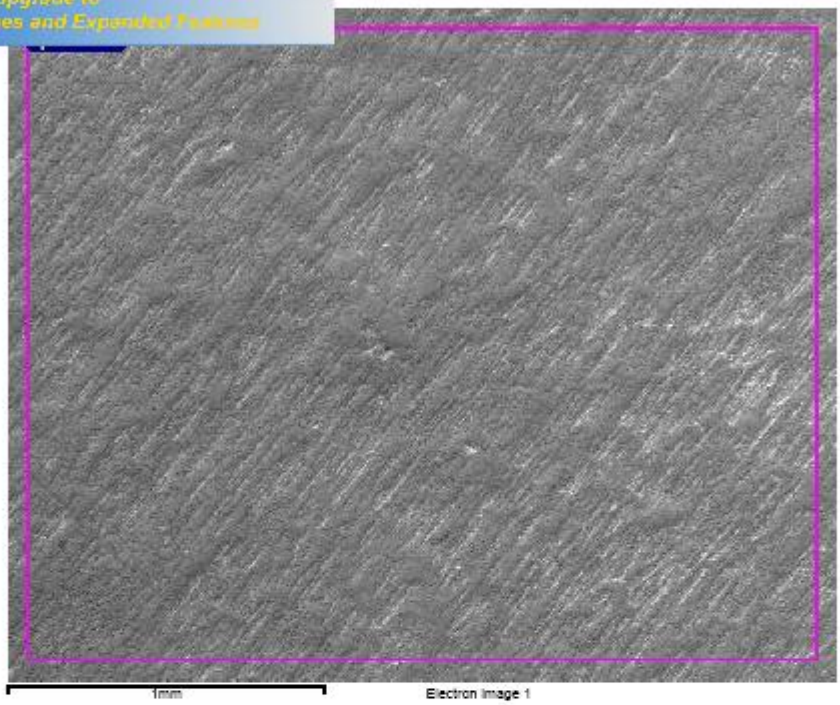
Element	Weight%	Atomic%
C K	16.22	48.77
O K	16.65	37.58
Si K	1.75	2.25
Pb M	65.38	11.40
Totals	100.00	

Comment: Pb II 105 x mag.

inca

Pb II: After Treatment at 103x

3/24/2011 3:17:38 PM



Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 2

Standard :
C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
Pb PbF2 1-Jun-1999 12:00 AM

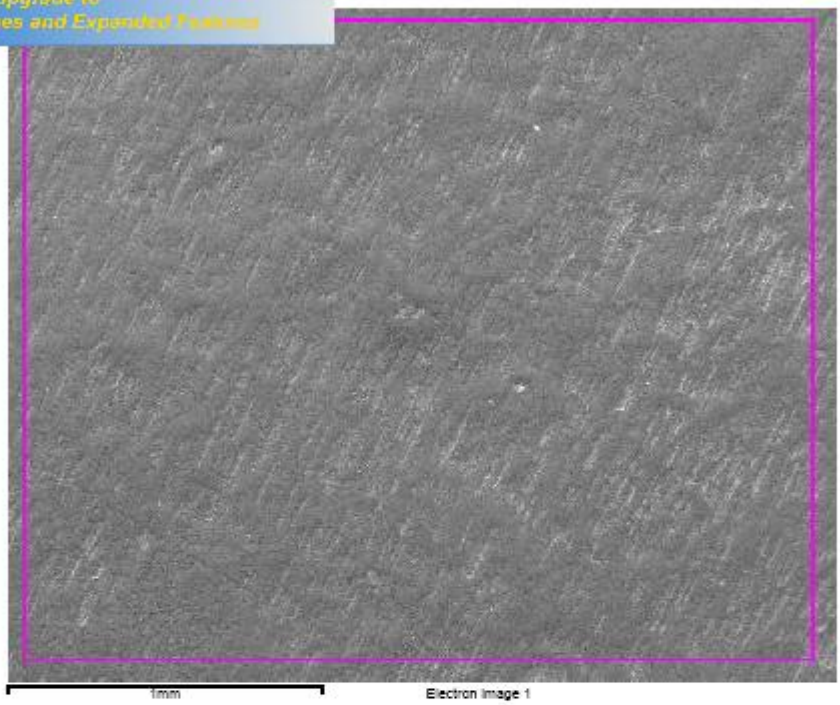
Element	Weight%	Atomic%
C K	11.35	61.35
O K	2.90	11.78
Pb M	85.74	26.86
Totals	100.00	

Comment: Pb II A.T. 103 x mag.

inca

Pb II: 2 Months After Treatment at 102x

5/6/2011 12:53:58 PM



Processing option : All elements analysed (Normalised)

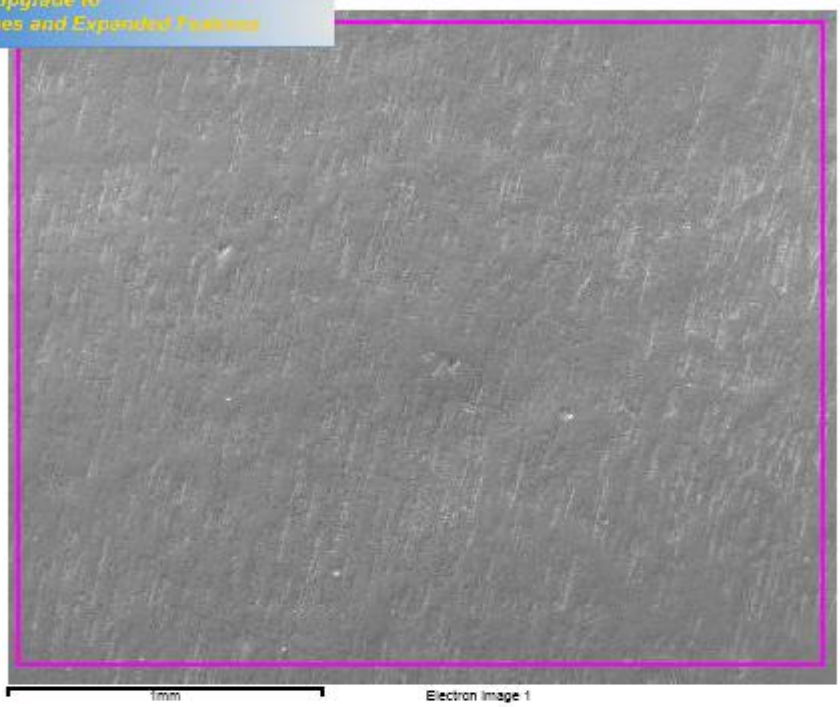
Spectrum	In stats.	O	Pb	Total
Spectrum 1	Yes	7.44	92.56	100.00
Mean		7.44	92.56	100.00
Std. deviation		0.00	0.00	
Max.		7.44	92.56	
Min.		7.44	92.56	

All results in weight%

inca

Pb II: 4 Months After Treatment at 103x

7/21/2011 11:38:37 AM



Processing option : All elements analysed (Normalised)

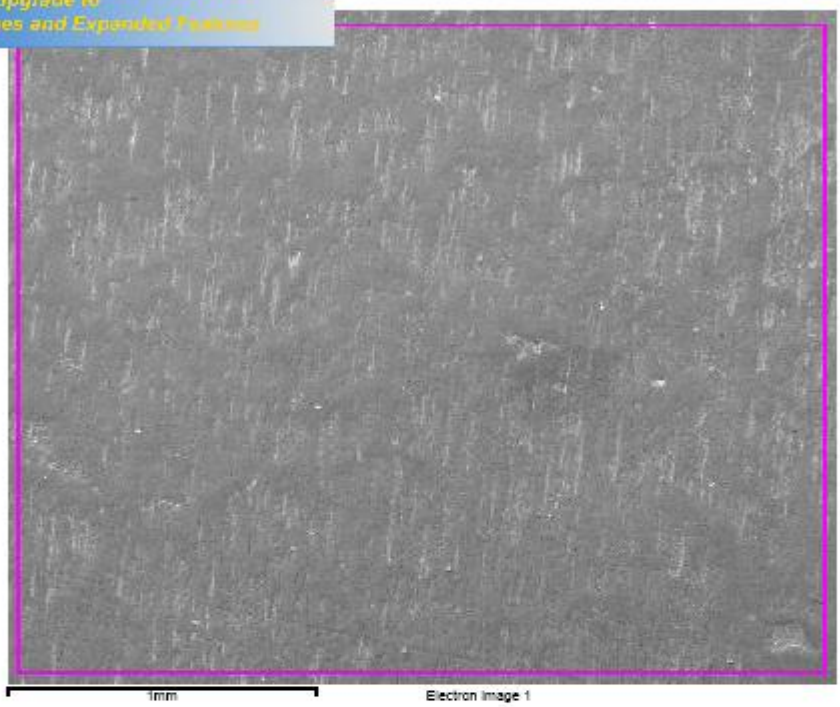
Spectrum	In stats.	C	O	Pb	Total
Spectrum 1	Yes	10.50	8.77	80.73	100.00
Mean		10.50	8.77	80.73	100.00
Std. deviation		0.00	0.00	0.00	
Max.		10.50	8.77	80.73	
Min.		10.50	8.77	80.73	

All results in weight%

inca

Pb II: 6 Months After Treatment at 100x

9/30/2011 3:36:11 PM



Processing option : All elements analysed (Normalised)

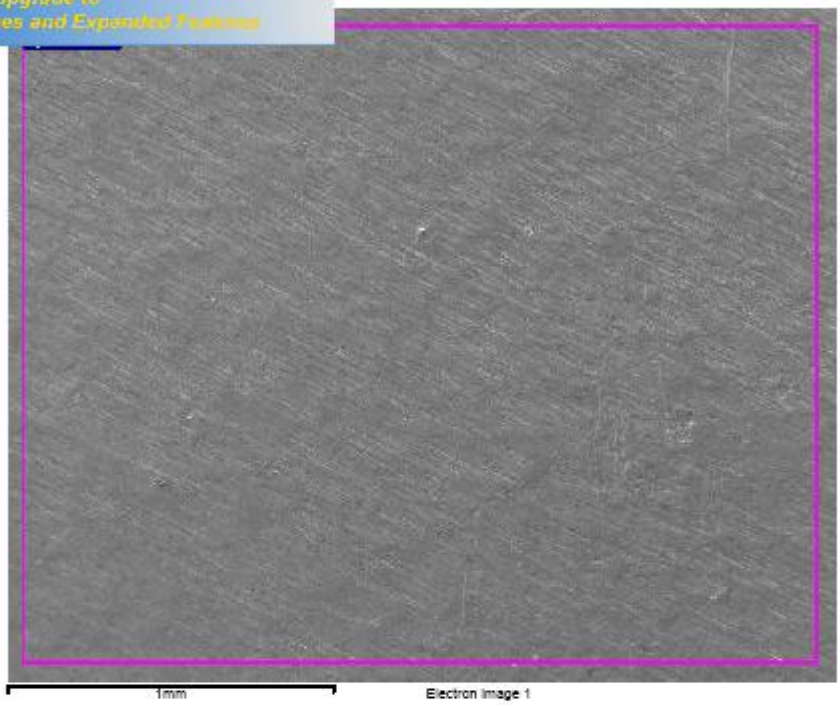
Spectrum	In stats.	C	O	Pb	Total
Spectrum 1	Yes	9.65	10.00	80.34	100.00
Mean		9.65	10.00	80.34	100.00
Std. deviation		0.00	0.00	0.00	
Max.		9.65	10.00	80.34	
Min.		9.65	10.00	80.34	

All results in weight%

inca

Pb III: Before Treatment at 106x

3/10/2011 12:53:21 PM



Processing option : All elements analysed (Normalised)

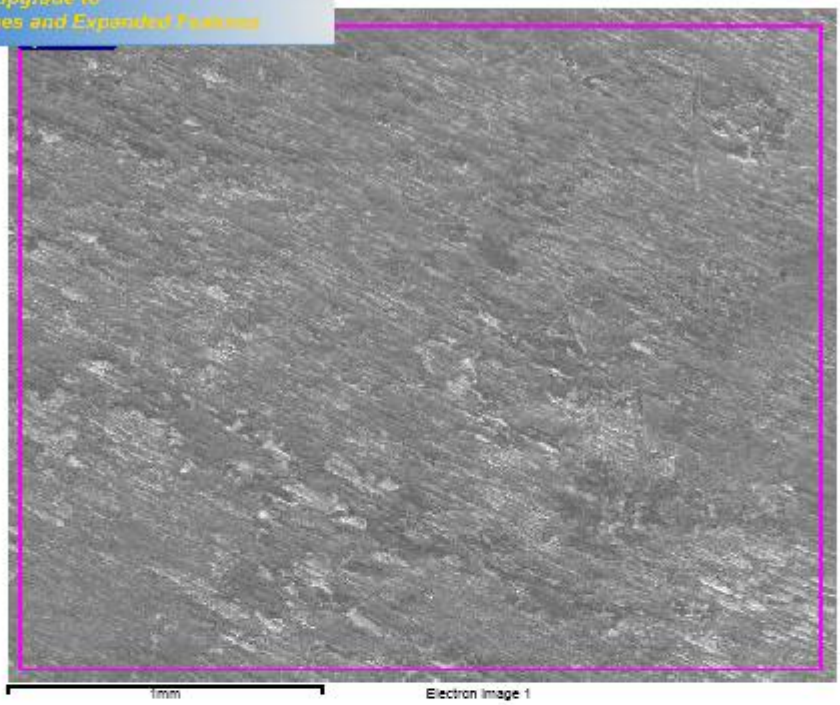
Spectrum	In stats.	C	O	Pb	Total
Spectrum 1	Yes	16.62	18.88	64.50	100.00
Mean		16.62	18.88	64.50	100.00
Std. deviation		0.00	0.00	0.00	
Max.		16.62	18.88	64.50	
Min.		16.62	18.88	64.50	

All results in weight%

inca

Pb III: After Treatment at 102x

3/24/2011 4:19:29 PM



Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 2

Standard :
C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
Pb PbF2 1-Jun-1999 12:00 AM

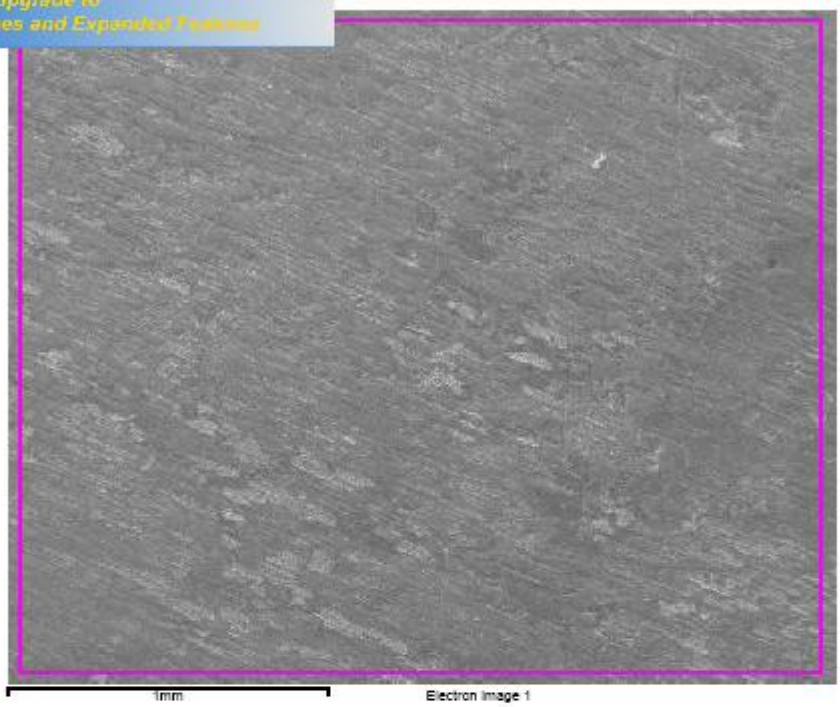
Element	Weight%	Atomic%
C K	14.02	59.62
O K	6.51	20.78
Pb M	79.47	19.60
Totals	100.00	

Comment: Pb III A.T. 102 x mag.

inca

Pb III: 2 Months After Treatment at 104x

5/23/2011 3:40:35 PM



Processing option : All elements analysed (Normalised)

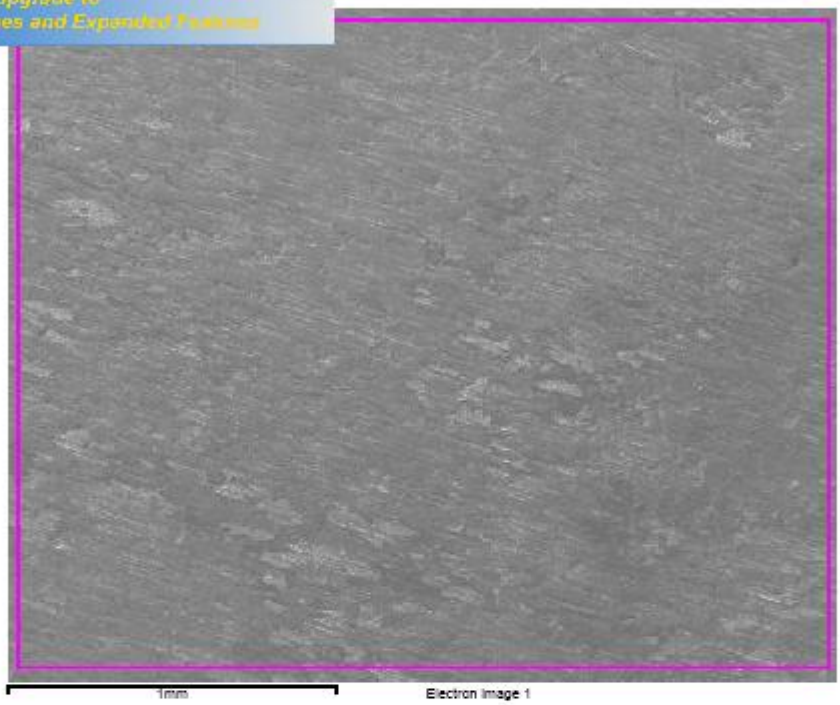
Spectrum	In stats.	C	O	Pb	Total
Spectrum 1	Yes	14.44	10.02	75.54	100.00
Mean		14.44	10.02	75.54	100.00
Std. deviation		0.00	0.00	0.00	
Max.		14.44	10.02	75.54	
Min.		14.44	10.02	75.54	

All results in weight%

inca

Pb III: 4 Months After Treatment at 107x

7/21/2011 12:20:04 PM



Processing option : All elements analysed (Normalised)

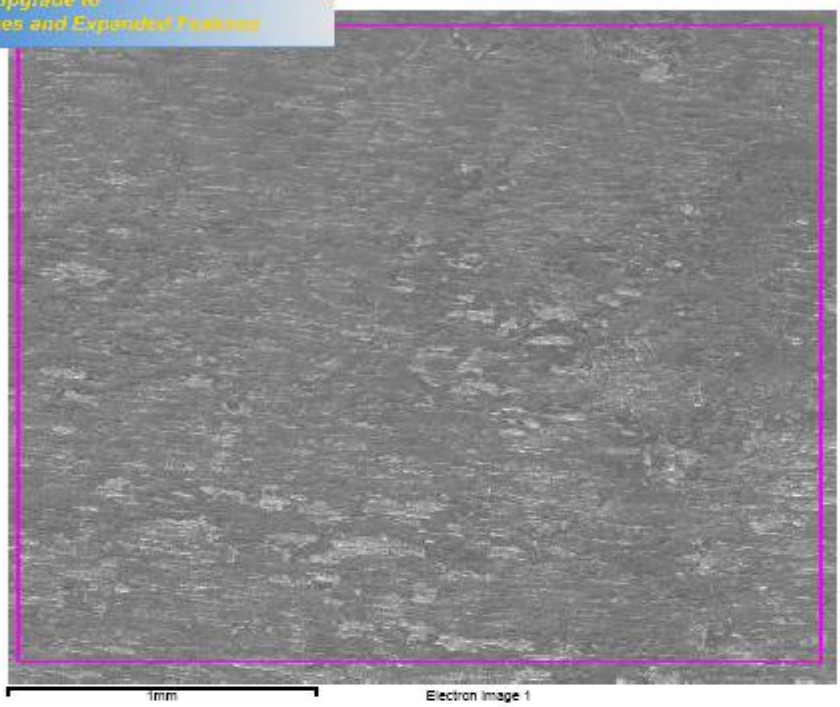
Spectrum	In stats.	C	O	Pb	Total
Spectrum 1	Yes	13.21	10.56	76.24	100.00
Mean		13.21	10.56	76.24	100.00
Std. deviation		0.00	0.00	0.00	
Max.		13.21	10.56	76.24	
Min.		13.21	10.56	76.24	

All results in weight%

inca

Pb III: 6 Months After Treatment at 100x

9/30/2011 4:06:05 PM



Processing option : All elements analysed (Normalised)

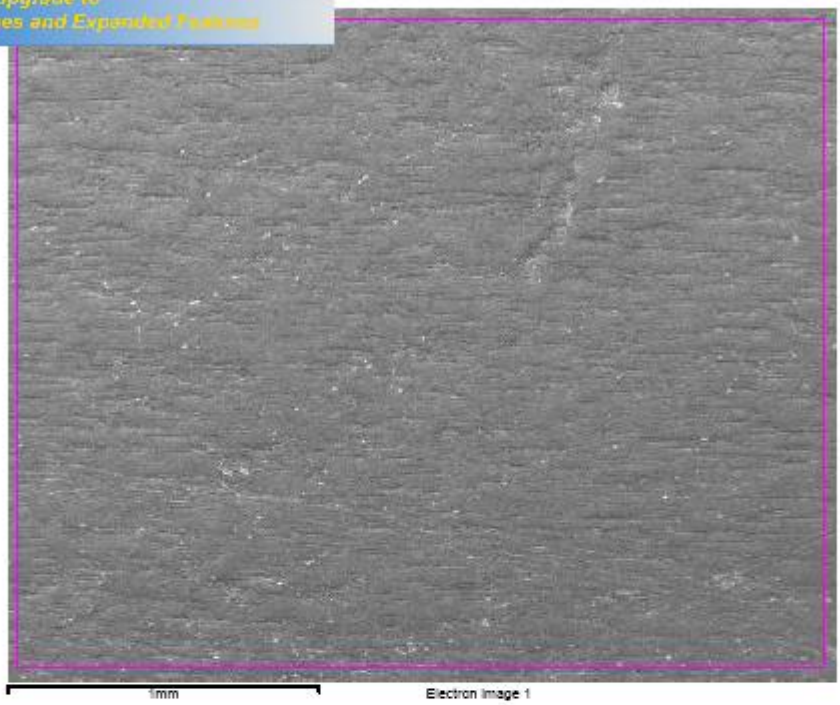
Spectrum	In stats.	C	O	Pb	Total
Spectrum 1	Yes	11.95	12.25	75.81	100.00
Mean		11.95	12.25	75.81	100.00
Std. deviation		0.00	0.00	0.00	
Max.		11.95	12.25	75.81	
Min.		11.95	12.25	75.81	

All results in weight%

inca

Pb IV: 2 Months After Treatment at 101x

5/23/2011 4:52:35 PM



Processing option : All elements analysed (Normalised)

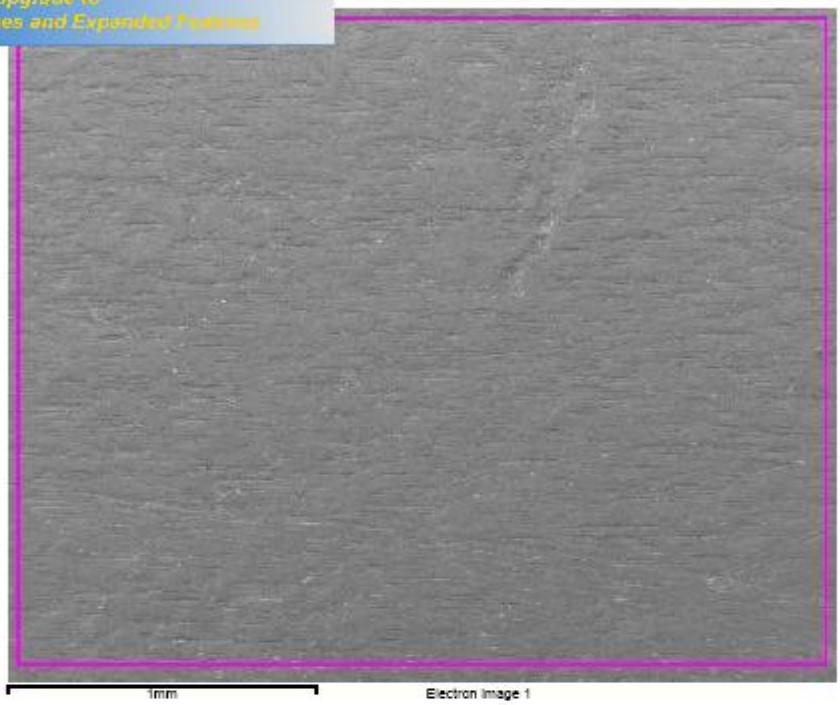
Spectrum	In stats.	C	O	Si	Pb	Total
Spectrum 1	Yes	15.16	17.25	0.86	66.74	100.00
Mean		15.16	17.25	0.86	66.74	100.00
Std. deviation		0.00	0.00	0.00	0.00	
Max.		15.16	17.25	0.86	66.74	
Min.		15.16	17.25	0.86	66.74	

All results in weight%

inca

Pb IV: 4 Months After Treatment at 100x

7/21/2011 2:09:54 PM



Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	O	Si	Pb	Total
Spectrum 1	Yes	12.45	18.25	0.85	68.46	100.00
Mean		12.45	18.25	0.85	68.46	100.00
Std. deviation		0.00	0.00	0.00	0.00	
Max.		12.45	18.25	0.85	68.46	
Min.		12.45	18.25	0.85	68.46	

All results in weight%

inca

Pb IV: 6 Months After Treatment at 102x

9/30/2011 4:49:24 PM

Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	O	Si	Pb	Total
Spectrum 1	Yes	10.60	18.84	0.84	69.72	100.00
Mean		10.60	18.84	0.84	69.72	100.00
Std. deviation		0.00	0.00	0.00	0.00	
Max.		10.60	18.84	0.84	69.72	
Min.		10.60	18.84	0.84	69.72	

All results in weight%

inca

6.2.5 ESEM-EDX Results for the Iron Alloy Coupons c. 100x

Fe I: Before Treatment at 107x

3/10/2011 2:31:41 PM

Processing option : All elements analysed (Normalised)

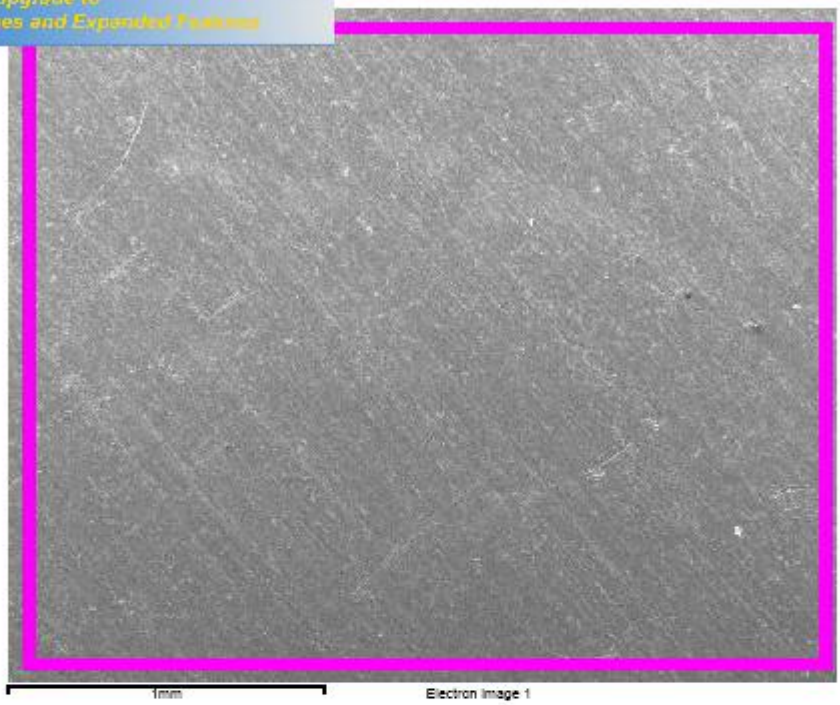
Spectrum	In stats.	C	Si	Fe	Total
Spectrum 1	Yes	7.10	0.58	92.33	100.00
Mean		7.10	0.58	92.33	100.00
Std. deviation		0.00	0.00	0.00	
Max.		7.10	0.58	92.33	
Min.		7.10	0.58	92.33	

All results in weight%

inca

Fe I: After Treatment at 103x

3/25/2011 11:12:35 AM



Processing option : All elements analysed (Normalised)

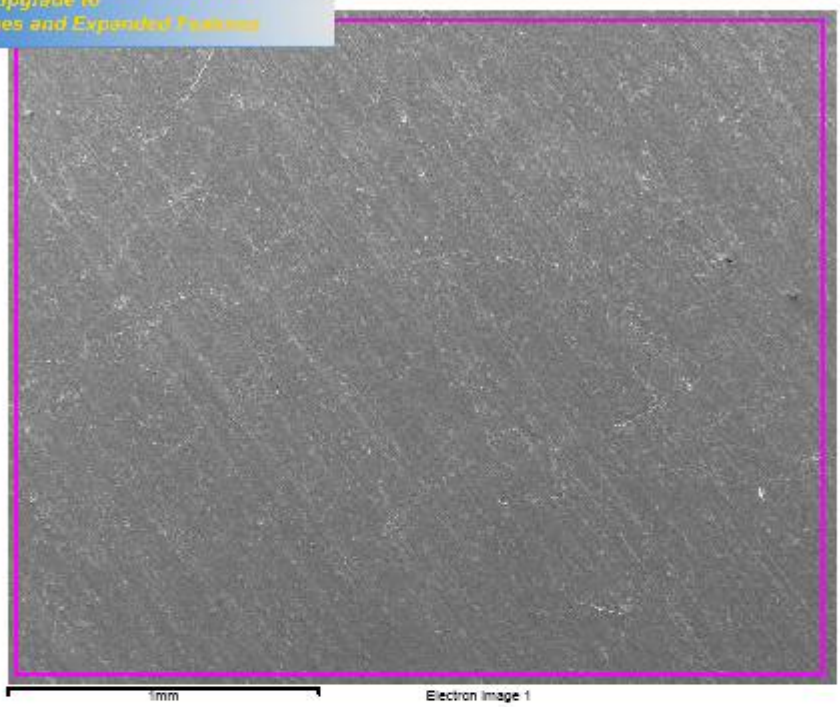
Spectrum	In stats.	C	Fe	Total
Spectrum 1	Yes	8.96	91.04	100.00
Mean		8.96	91.04	100.00
Std. deviation		0.00	0.00	
Max.		8.96	91.04	
Min.		8.96	91.04	

All results in weight%

inca

Fe I: 2 Months After Treatment at 102x

5/25/2011 10:55:19 AM



Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	Fe	Total
Spectrum 1	Yes	8.60	91.40	100.00
Mean		8.60	91.40	100.00
Std. deviation		0.00	0.00	
Max.		8.60	91.40	
Min.		8.60	91.40	

All results in weight%

inca

Fe I: 4 Months After Treatment at 104x

7/21/2011 4:10:04 PM

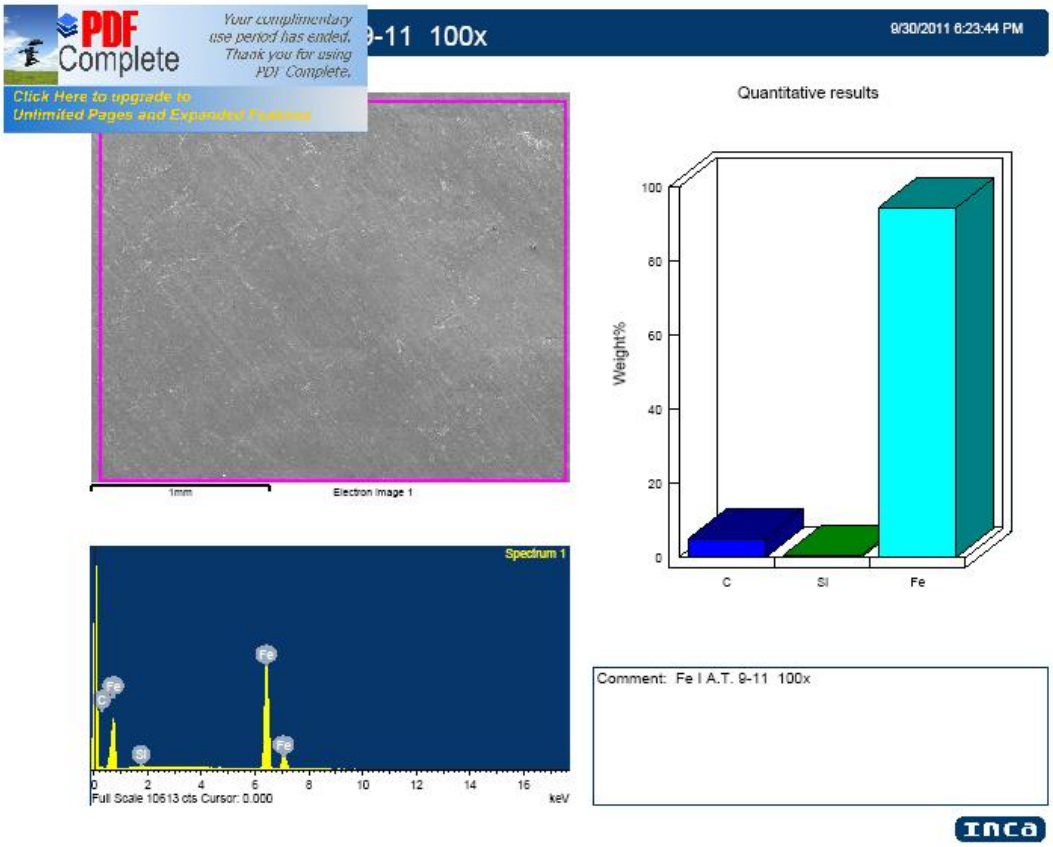
Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	Al	Si	Fe	Total
Spectrum 1	Yes	7.47	0.30	0.52	91.70	100.00
Mean		7.47	0.30	0.52	91.70	100.00
Std. deviation		0.00	0.00	0.00	0.00	
Max.		7.47	0.30	0.52	91.70	
Min.		7.47	0.30	0.52	91.70	

All results in weight%

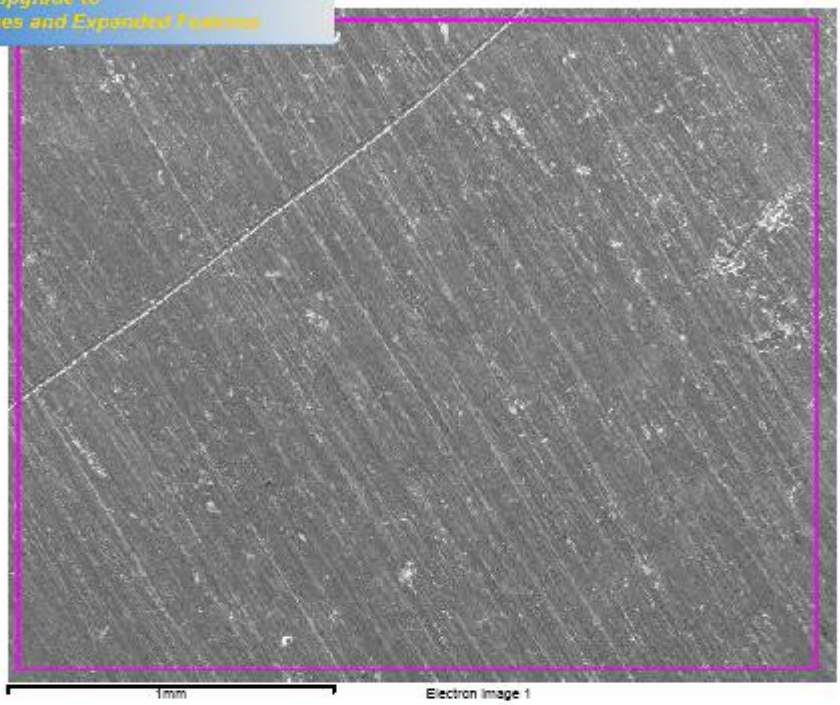
inca

Fe I: 6 Months After Treatment at 100x



Fe II: Before Treatment at 106x

3/10/2011 3:20:02 PM



Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 2

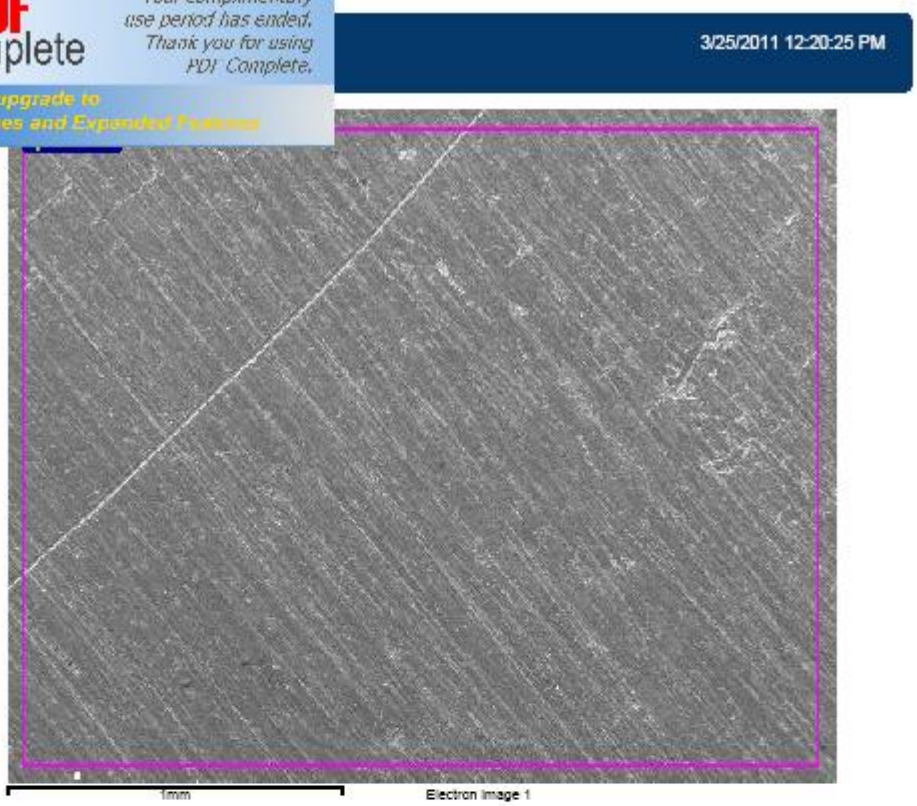
Standard :
C CaCO3 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
Fe Fe 1-Jun-1999 12:00 AM
Br KBr 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	7.17	26.41
Si K	0.59	0.93
Fe K	90.79	71.86
Br L	1.45	0.80
Totals	100.00	

Comment: Fe II B.T. - 106 x mag.

inca

Fe II: After Treatment at 109x



Processing option : All elements analysed (Normalised)

Spectrum	In stats.	Si	Fe	Total
Spectrum 1	Yes	1.19	98.81	100.00
Mean		1.19	98.81	100.00
Std. deviation		0.00	0.00	
Max.		1.19	98.81	
Min.		1.19	98.81	

All results in weight%

inca

Fe II: 2 months After Treatment at 101x

5/25/2011 12:13:10 PM

Processing option : All elements analysed (Normalised)

Spectrum	In stats.	Al	Si	Fe	Total
Spectrum 1	Yes	0.65	0.75	98.60	100.00
Mean		0.65	0.75	98.60	100.00
Std. deviation		0.00	0.00	0.00	
Max.		0.65	0.75	98.60	
Min.		0.65	0.75	98.60	

All results in weight%

inca

Fe II: 4 months After Treatment at 102x

7/21/2011 4:46:45 PM

Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	Al	Si	Fe	Total
Spectrum 1	Yes	5.87	0.67	0.79	92.67	100.00
Mean		5.87	0.67	0.79	92.67	100.00
Std. deviation		0.00	0.00	0.00	0.00	
Max.		5.87	0.67	0.79	92.67	
Min.		5.87	0.67	0.79	92.67	

All results in weight%

inca

Fe II: 6 months After Treatment at 102x

9/30/2011 11:25:29 AM

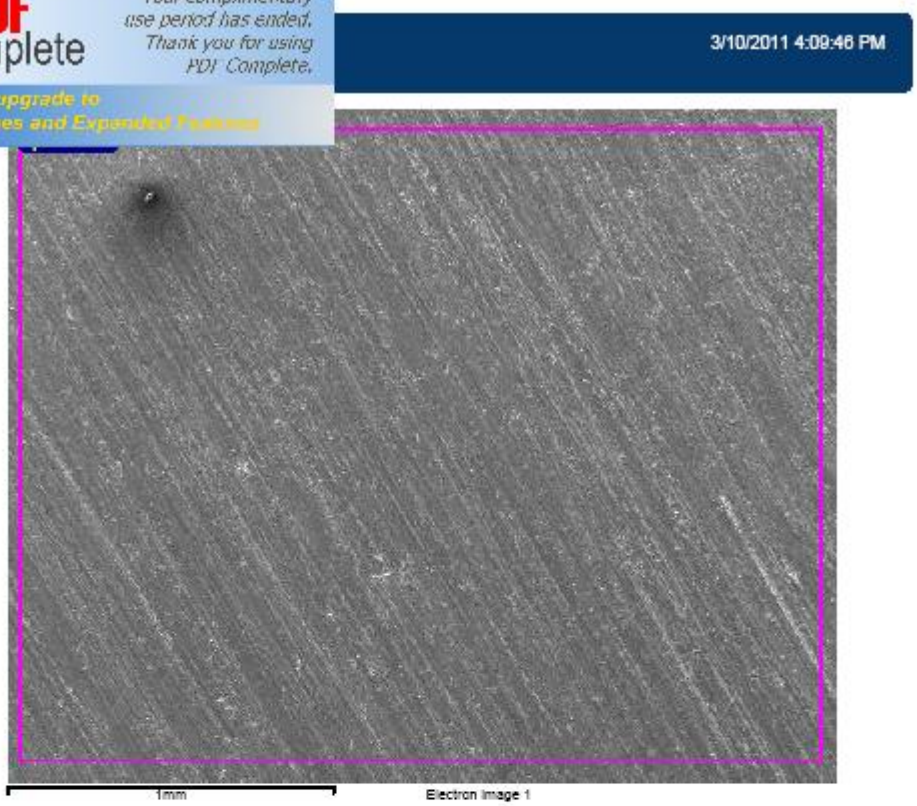
Processing option : All elements analysed (Normalised)

Spectrum	In stats.	Si	Fe	Br	Total
Spectrum 1	Yes	0.82	97.75	1.44	100.00
Mean		0.82	97.75	1.44	100.00
Std. deviation		0.00	0.00	0.00	
Max.		0.82	97.75	1.44	
Min.		0.82	97.75	1.44	

All results in weight%

inca

Fe III: Before Treatment at 106x



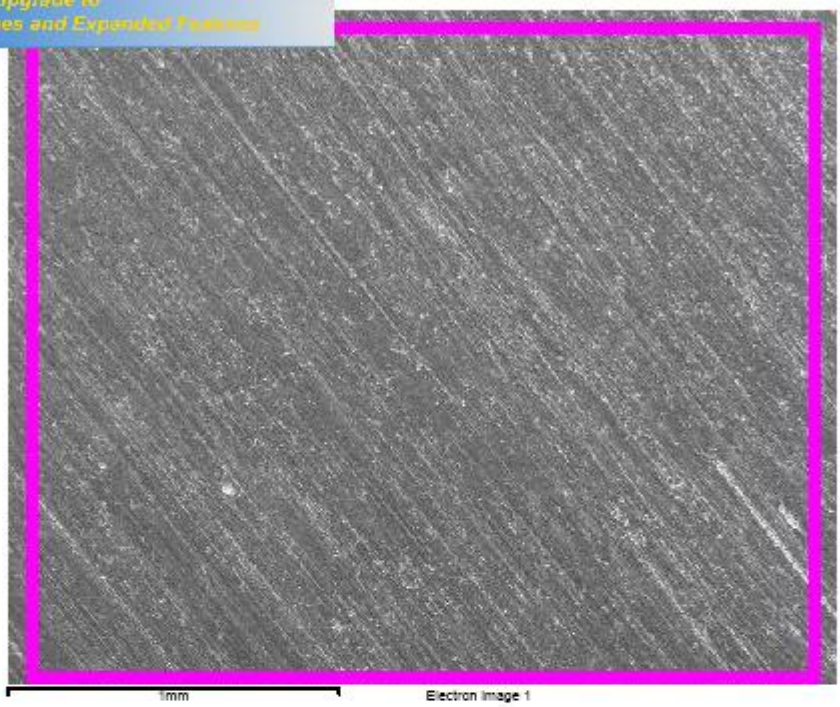
Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	Si	Fe	Total
Spectrum 1	Yes	7.78	1.22	91.00	100.00
Mean		7.78	1.22	91.00	100.00
Std. deviation		0.00	0.00	0.00	
Max.		7.78	1.22	91.00	
Min.		7.78	1.22	91.00	

All results in weight%

Fe III: After Treatment at 108x

3/25/2011 1:23:55 PM



Processing option : All elements analysed (Normalised)

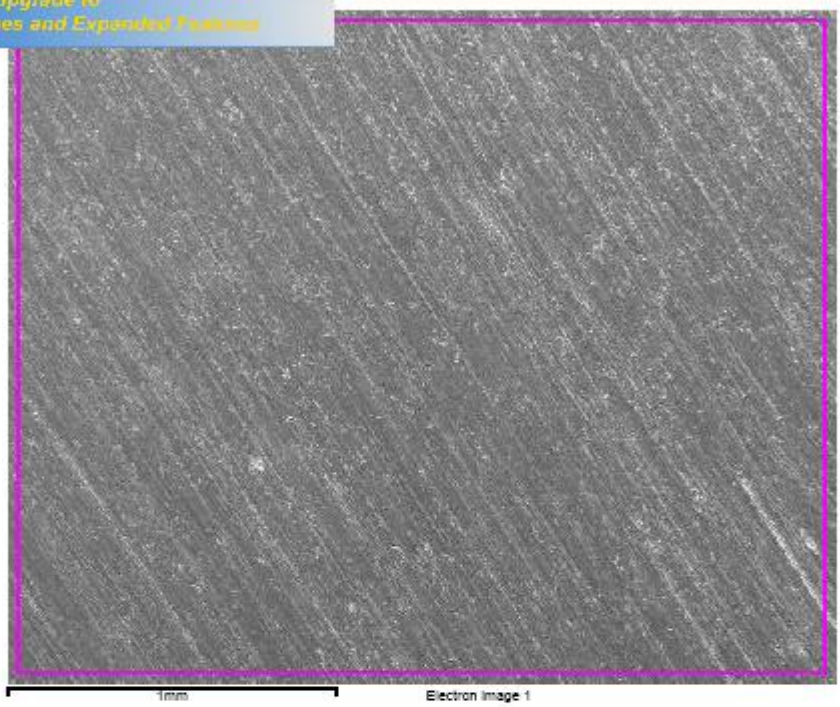
Spectrum	In stats.	Si	Fe	Total
Spectrum 1	Yes	1.68	98.32	100.00
Mean		1.68	98.32	100.00
Std. deviation		0.00	0.00	
Max.		1.68	98.32	
Min.		1.68	98.32	

All results in weight%

inca

Fe III: 2 Months After Treatment at 107x

5/25/2011 3:13:14 PM



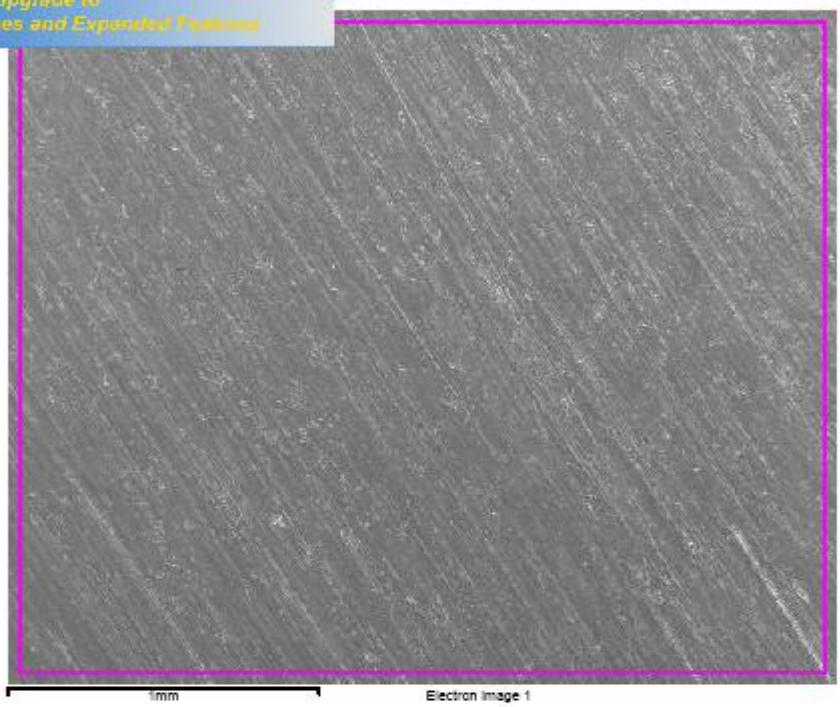
Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	Si	Fe	Total
Spectrum 1	Yes	7.04	1.49	91.47	100.00
Mean		7.04	1.49	91.47	100.00
Std. deviation		0.00	0.00	0.00	
Max.		7.04	1.49	91.47	
Min.		7.04	1.49	91.47	

All results in weight%

Fe III: 4 Months After Treatment at 102x

7/21/2011 5:28:30 PM



Processing option : All elements analysed (Normalised)

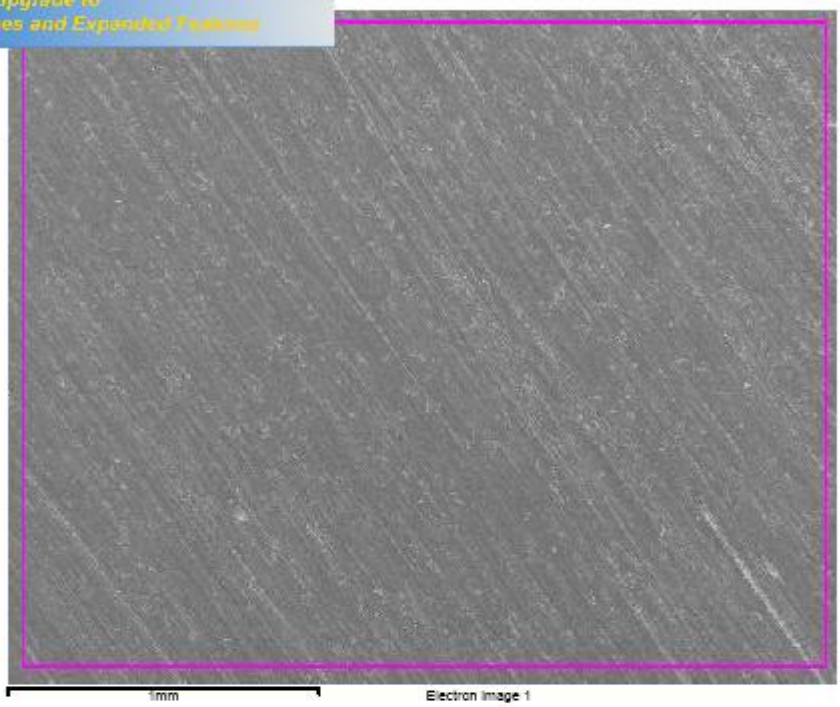
Spectrum	In stats.	C	Si	Fe	Total
Spectrum 1	Yes	6.38	1.48	92.15	100.00
Mean		6.38	1.48	92.15	100.00
Std. deviation		0.00	0.00	0.00	
Max.		6.38	1.48	92.15	
Min.		6.38	1.48	92.15	

All results in weight%

inca

Fe III: 6 Months After Treatment at 102x

9/30/2011 12:13:46 PM



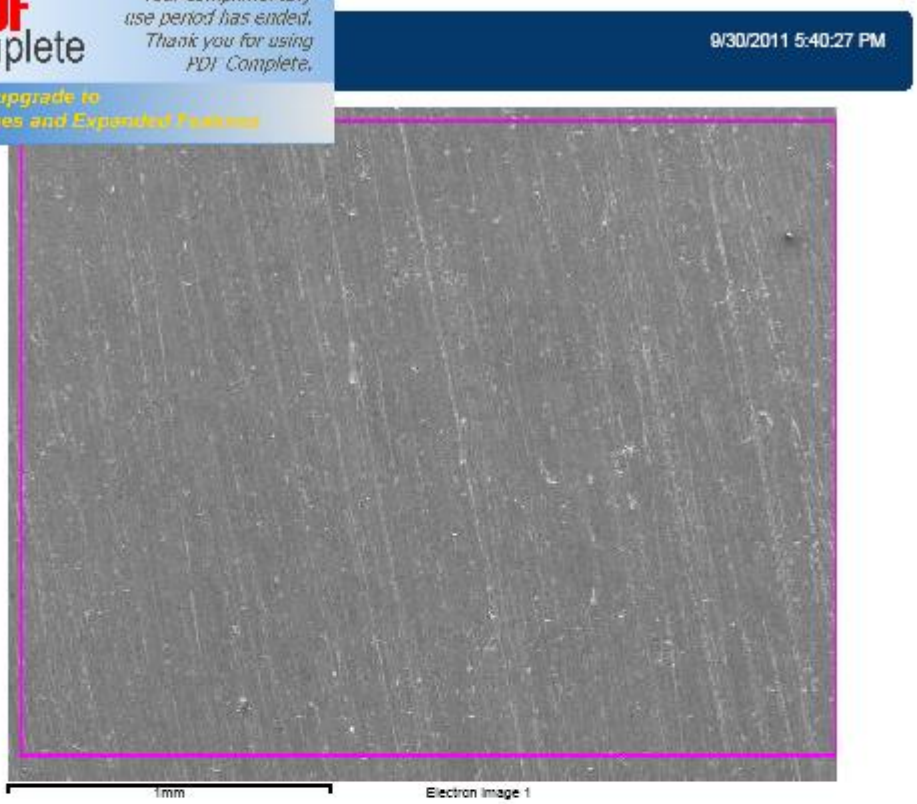
Processing option : All elements analysed (Normalised)

Spectrum	In stats.	Si	Mn	Fe	Total
Spectrum 1	Yes	1.83	0.73	97.44	100.00
Mean		1.83	0.73	97.44	100.00
Std. deviation		0.00	0.00	0.00	
Max.		1.83	0.73	97.44	
Min.		1.83	0.73	97.44	

All results in weight%

INCA

Fe IV: Control at 105x



Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	Si	Fe	Total
Spectrum 1	Yes	4.46	1.66	93.88	100.00
Mean		4.46	1.66	93.88	100.00
Std. deviation		0.00	0.00	0.00	
Max.		4.46	1.66	93.88	
Min.		4.46	1.66	93.88	

All results in weight%

inca

7.0 Materials and Suppliers

7.1 Non-Invasive Characterisation of a Collection of Modern Religious Medals using Portable X-ray Fluorescence Spectroscopy

7.2 Analysing the Effects of Cleaning Treatments in Metals Conservation with Scanning Electron Microscopy - Energy Dispersive X-ray Spectroscopy

7.1 Non-Invasive Characterisation of a Collection of Modern Religious Medals using Portable X-ray Fluorescence Spectroscopy

The following metal reference standards used to check the calibration of the Thermo Scientific Niton XL 3t pXRF analyser were supplied by:

Goodfellow Cambridge Ltd
Ermine Business Park, Huntingdon, England PE29 6WR
Email: **info@goodfellow.com**
Telephone: 0800 731 4653 (UK) or +44 1480 424 800
Fax: 0800 328 7689 (UK) or +44 1480 424 900
http://www.goodfellow.com/

Silver: 99.9 % - 25 x 25 x 1.5 mm
Copper: 99.95 % - 150 x 150 x 0.7 mm
Brass: Cu 63 % Zn 37 % - 150 x 150 x 0.5 mm
Bronze: Cu 94 % Sn 6 % - 150 x 150 x 0.25 mm
Iron: 99.5 % - 150 x 150 x 3.0 mm
Zinc: 99.99 % - 25 x 25 x 3.0 mm

7.2 Analysing the Effects of Cleaning Treatments in Metals Conservation with Scanning Electron Microscopy - Energy Dispersive X-ray Spectroscopy

The silver, copper and lead coupons used as samples in the ESEM-EDX analysis of the effects of cleaning treatments in metals conservation were supplied by:
Arkivprodukter AS
Fr. Nansensgate 32
2319 Hamar
Norway
Telephone: +47 926 51 375
Email: post@arkivprodukte.no
http://www.arkivprodukter.no/

The iron coupons used as samples in the ESEM-EDX analysis of the effects of cleaning treatments in metals conservation were supplied by Henning Schulze, Senior Lecturer

and Programme Leader for the BA Honours Degree in the Conservation Training Programme at the University of Lincoln.

The proprietary products and materials used in the conservation preparations in the research component analysing the effects of cleaning treatments in metals conservation with ESEM-EDX are listed below and the manufacturers/suppliers are given, as well as the online reference for the materials safety data sheets and product information. Small samples of the Goddard's Silver Dip, Silvo Silver Polish, Liberon Brass and Copper Polish and Renaissance De-Corroder from the reference collection in the Conservation Training Programme at the University of Lincoln were supplied by Henning Schulze, Senior Lecturer and Programme Leader for the BA Honours Degree in Conservation, for use in the experimental work for the Research MSc, so that the results could be presented to the conservation students and they would be familiar with the products analysed.

Goddard's Silver Dip:
SC Johnson Ltd
Frimley Green
Frimley
CAMBERLEY
Surrey
GU16 7AJ
T: +44 01276 852000
F: +44 01276 852 295.
http://www.scjohnson.co.uk/ngcontent.cfm?a_id=6010
MSDS: http://whatsinproducts.com/files/brands_pdf/1330626281.pdf
Product Information: http://hpd.nlm.nih.gov/cgi-bin/household/brands?tbl=brands&id=14008005

Silvo Silver Polish:
Reckitt Benckiser
Turner House
103-105 Bath Road
Slough
Berkshire SL1 3UH
U.K.

T: +44 (0)1753 217800

F: +44 (0)1753 217899

http://www.rb.com/rb-worldwide

MSDs: http://huntind.com.au/wp-content/uploads/2013/07/silvo_silver_polish.pdf

Product Information: http://www.rbanzinfo.com.au/dyn/IngredientsList?productID=1015

Precipitated Calcium Carbonate:

Sigma-Aldrich Norway AS

C/O Aker Brygge Business Centre P.B. 1433 Vika

0115 Oslo

Norway

T: +47 23 17 60 60

F: +47 23 17 60 10

Email: NordicOrder@sial.com

http://www.sigmaaldrich.com/norway/kontaktinformasjon.html

http://www.mineralstech.com/fileadmin/user_upload/mti/MSDS/cmsat2020lifspcc_Standard.pdf

MSDS:

http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=GB&language=en&productNumber=21061&brand=SIGMA&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Fsigma%2F21061%3Flang%3Den

Liberon Brass and Copper Polish:

Liberon Limited

Learoyd Road

Mountfied Industrial Estate

New Romney

Kent TN28 8XU

U.K.

T: +44 01797 367555

F: +44 01797 367575

http://www.liberon.co.uk/

MSDS: http://www.liberon.co.uk/metal-treatments/gallery_files/site/2136/7731/7736/19732.pdf

Product Information: http://www.liberon.co.uk/metal-treatments/brass-and-copper-polish,434,464.html?&args=Y29tcF9pZD0zMDQmYWN0aW9uPWZpY2hlUHJvZHVpdCZpZD0yNTUmfA%3D%3D

Nevr Dull Wadding Polish:

The George Basch Co. Inc

19 Hanse Ave

P.O. Box 188

Freeport

NY 11520

T: +1 516 378 8100

MSDS: http://www.nevrdull.com/MSDS.htm

Product Information: http://cool.conservation-us.org/byform/mailing-lists/cdl/2004/0174.html

Available at Amazon.co. uk

http://www.amazon.co.uk/NEVR-DULL-553-22-88-mirror-polishing-wadding--Content/dp/B00BY2C2PE/ref=sr_1_2?ie=UTF8&qid=1376333497&sr=8-2&keywords=nevr+dull+wadding+polish

Pre-Lim Surface Cleaner:

Picreator Enterprises Ltd.

4 Park View Gardens

Hendon

London

NW4 2PN

U.K:

T : +44 (0)208 202 8972
F : +44 (0)208 202 3435
Email: info@picreator.co.uk

MSDS: http://www.productosdeconservacion.com/pdf/prelim.pdf

Product Information: http://www.picreator.co.uk/articles/4_pre_lim_surface_clea.htm

Disodium ethylenediaminetetraacetate dehydrate (EDTA):

Sigma-Aldrich Company Ltd.

The Old Brickyard

New Road

Gillingham

Dorset SP8 4XT

U.K.

T: + 44 0800 717181

F: + 44 0800 378785

E-mail: ukorders@sial.com

MSDS:

http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=GB&language=en&productNumber=E4884&brand=SIAL&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Fsial%2Fe4884%3Flang%3Den

Methyl Cellulose

Preservation Equipment Ltd.

Vinces Road
Diss
Norfolk IP22 4HQ
U.K.
T: +44 01379 647400
F: +44 0 1379 650582
Email: info@preservationequipment.com
MSDS:

http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=GB&language=en&productNumber=M0387&brand=SIGMA&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Fsigma%2Fm0387%3Flang%3Den

Product Information: http://www.preservationequipment.com/Store/Products/Conservation-Materials/Mounting-$4-Framing/Methyl-Cellulose

Renaissance De-Corroder:

Picreator Enterprises Ltd.

4 Park View Gardens

Hendon

London NW4 2PN

U.K:

T : +44 (0)208 202 8972

F : +44 (0)208 202 3435
Email: info@picreator.co.uk
MSDS: http://www.kremer-pigmente.com/media/files_public/62902_SHD_ENG.pdf

Product Information: http://www.picreator.co.uk/articles/10_renaissance_metal_de.htm